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DESCRIPTION OF A BOMB-CALORIMETER AND METHOD OF ITS USE.

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THE apparatus of which an account is here given was first described in 1895.[1] The present description is, in part, a revision of one published in 1897.[2] Experience since the latter article was written has led to further improvements in the bomb and accessory apparatus. A number of the improvements have been devised by Mr. Blakeslee, formerly mechanician of Wesleyan University; others were suggested by Dr. F. G. Benedict, who has had much to do with its use, and by Messrs. Dinsmore and Singleton, of Middletown, Conn., by whom the apparatus is now made.

The bomb is a modification of that of Berthelot.[3] The latter is most excellent; the only objection to it is its great cost, which is due to the large amount of platinum in the cover and lining.

[1] "A New Form of Bomb-Calorimeter," by W. O. Atwater and Chas. D. Woods. Report of the Storrs (Conn.) Experiment Station for 1894, p. 135.

[2] "Improved Forms of Bomb-Calorimeter and Accessory Apparatus," by W. O. Atwater and O. S. Blakeslee. Report of the Storrs (Conn.) Experiment Station for 1897, p. 199.

[3] "Sur la force des matières explosives," I, 225 and *Ann. chim. phys.*, (6) **6**, 546.

Various modifications of the Berthelot apparatus have been devised to obviate the expense of the platinum. Mahler uses a bomb of forged steel, with enamel lining. Hempel uses, for the determination of heats of combustion of coal, a simple bomb of steel without lining. In accordance with suggestions by one of us (W. O. A.) during a sojourn in Dresden, Professor Hempel most kindly had a bomb made by the mechanicians who make the bombs of his devising, and lined by Heraeus of Hanau with a thin sheet of platinum. Thanks to Professor Hempel's painstaking care, added to his inventive skill and his familiarity with the subject, the bomb proved very efficient. With modifications from time to time, it has gradually assumed its present form. The principle is the same as in Berthelot's bomb, but whereas the cover of Berthelot's fits into the cylindrical cup like a very wide stopper, the cover in this, as in Mahler's, rests directly on the upper edge of the cup.

The purpose of the present article is to describe the bomb and accessory apparatus and the method of their use in the determination of the heats of oxidation of foods, feeding-stuffs and products of animal metabolism, a kind of work for which the apparatus has been in almost constant use in this laboratory for some ten years. Experience here and elsewhere shows that the apparatus may be advantageously employed for determining sulphur and phosphorus in organic compounds, as well as for determining the heats of combustion of coal and other fuel materials, but the special ways by which it is best employed for these purposes will be more fitly described at another time.

The method of determining heats of combustion is essentially the procedure of Berthelot as modified by Stohmann.[1] It has been gradually developed in this laboratory under the hands of Messrs. C. D. Woods, F. G. Benedict, O. F. Tower and the authors.

I. DESCRIPTION OF THE APPARATUS.

The method consists essentially in burning the substance in excess of oxygen at high pressure in a bomb immersed in water, the heat of combustion being determined by the rise in the temperature of the water. The apparatus consists of:

(1) The calorimeter proper, including the bomb, a britannia-metal cylinder to hold the water in which the bomb is immersed, a thermometer and a stirrer. The term *calorimeter system* is here

[1] *J. prakt. Chem.*, **147**, 503 (1889). See also Berthelot: "Traité pratique de calorimètrie chimique," p. 128.

used to denote the bomb and contents, the metal cylinder and the immersed parts of the thermometer and stirrer, together with the water.

(2) Two concentric protecting-cylinders of "indurated fiber" with cover. These enclose the calorimeter system and insulate it so as to prevent rapid passage of heat between it and the outside air.

(3) Accessory apparatus, including a clamp and spanner for closing the bomb, appliances for filling the bomb with oxygen (bomb-support, coupling and manometer), a mould and press for moulding powdered substances, which are to be burned, into pellets, electrical appliances for igniting the charge, and machinery for operating the stirrer.

The Bomb.

The bomb consists of three parts: A cylindrical *cup* to contain

Fig. 1.—Parts of the bomb. Cup, cover with capsule holder, capsule and collar.

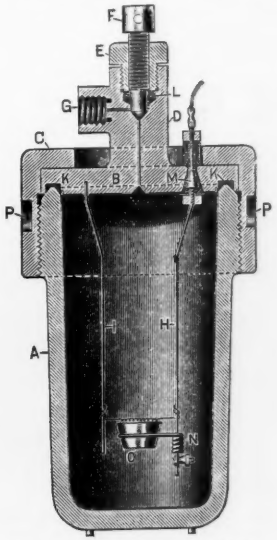

Fig. 2.—Cross-section of the bomb.

the substance to be burned and the oxygen for combustion, a *cover* to close the cup, and a threaded ring or *collar* to hold the cover tightly on the cylinder. With these is a metal capsule to hold the substance. The parts are shown separately in Fig 1, and in cross-section, as put together, in Fig. 2.

The cup is of Hotchkiss gun tool steel, kindly furnished by the Bethlehem Iron Company, which has favored us with tests of "oil-tempered forgings made from the same steel, and at about the same time the bars were made" which were used for the later bombs. These latter tests "were many in number, and an average taken from them gives the following results":

Tensile strength	85,514 lbs. per sq. in.
Elastic limit	47,366 " " " "
Extension	23.82 per cent.
Contraction	43.05 per cent.

The cover (B), collar (C), and screws (E, F) are of the best tool steel.

In the apparatus as now made the inside dimensions of the cup are, approximately: Depth, 12.7 cm.; diameter, 6.3 cm. at top and 5.9 cm. at bottom. The wall is approximately 0.6 cm. in thickness. The weight of the whole bomb is not far from 3,200 grams, and its capacity nearly 380 cc.

The cover is lined on the bottom with platinum and is provided with a neck (D). Into this fits, at the top, a cylindrical screw (E), into which in turn fits a valve screw (F). In the neck (D), where the bottom of the cylindrical screw (E) rests, is a shoulder fitted with a packing of lead (L). The pressure of the valve screw on this packing makes a tight closure upon the part of F which it surrounds. On the side of D is an opening (G), into which may be screwed the coupling connecting the tube with the receptacle which holds the oxygen used for the combustion (see Fig. 8). The coupling, when screwed in, thrusts against a washer of lead at the end of G, which insures perfect closure. A narrow passage runs horizontally to a point just above the valve seat in the center of D. A similar passage runs from the apex of the valve seat perpendicularly downwards through the cover. These two passages provide a channel for the oxygen to pass into the interior of the bomb. This channel may be tightly closed by the valve screw, the lower end of which is conical and thrusts against the inner surface of D, the angle of which at the place of contact corresponds to that of the tip of the screw. Between the top of the valve seat and the bottom of the packing (L), the valve screw fits so closely in the cover as to prevent the lead of the packing from working downward and thus obstructing the small gas passages. After continued use, the valve of the bomb may be

found to leak a little on account of corrosion of the conical end of the valve screw by nitric acid and moist oxygen. It should then be reseated by an expert mechanician. The lead washer (G) and valve packing (L) will require to be replaced after long use.

The upper edge of the cup (A) is beveled on both sides; the apex is rounded and fits into a gasket (K) of lead, which is held in a recess or groove in the cover (B). With use, the metal gradually flows out of the groove under the heavy pressure so that the gaskets have to be replaced occasionally. The gasket may be removed from the groove in the cover by cutting it nearly in two with the tool provided for the purpose and prying it up in such way as to sever it. In using the tool, great care must be taken not to injure either the platinum lining of the cover or the sides and bottom of the groove. Attempts have been made to substitute harder metals for lead in the gaskets, but lead has been found most satisfactory as least liable to injure the platinum lining against which it presses. Extra gaskets are furnished with the bomb. In closing the bomb, it is important that the friction between the cover and collar should be reduced as much as possible. The surfaces of contact of the two pieces should, therefore, be well oiled.

The platinum wires (H) and (I), inside the bomb, serve to hold the capsule (O) containing the substance to be burned and to conduct an electric current for igniting it. Of these two wires, one (I) is screwed into the cover; the other (H) passes through a conical hole in the cover and is insulated from the metal. The method of insulating the wire is shown in Fig. 3. In the bomb

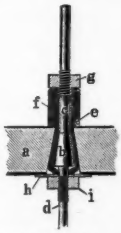

Fig. 3.—Method of insulation.

cover, a section of which is shown at a, is a conical hole. The larger end of the hole is on the inside of the cover. Into the hole fits the conical enlargement (b) of the German silver rod (c) which projects above the cover and serves for the electrical connection. The platinum wire (d) is gold-soldered into the lower

end of the cone, thus making a continuous conductor (c, b, d). To insulate this conductor, a piece of rubber tubing of $^3/_{32}$ inch (2.5 mm.) inside diameter is pushed down over the cone until it projects 1 to 2 mm. beyond the base. The free end of the tubing is threaded through the hole in the bomb cover and drawn up until the cone is in place; the surplus rubber tubing is then cut off at e, and over the rod (c) is placed the hard rubber sleeve (f) and the nut (g) is tightened down until the conductor (c, b, d) is firm in the cover. A mica disk (h) is placed over the platinum wire (d), and held against the lining of the cover by the platinum nut (i). This disk serves both to protect the insulating rubber from combustion and to prevent the nitric acid formed in the bomb from penetrating into the conical hole in the cover and causing leakage of current and corrosion of the German silver and steel. If a little space at the large end of the cone is left unfilled by the end of the rubber tubing, it is filled with a mixture of fine asbestos fiber and shellac, which is allowed to dry before the mica disk (h) is secured in place. Whenever the insulation of the wire becomes poor, the rubber covering of the conductor should be replaced by a new one.

Near the lower end of H (Fig. 2) is a platinum wire bent in the form of a ring to hold the capsule, and coiled about the wire, to which it is held by a platinum thumb-nut. When a combustion is made, the two platinum wires are connected by a very fine iron wire which passes over the capsule and is heated by the electric current. The part directly above the substance to be burned is wound into a spiral, thus furnishing a larger quantity of iron to be ignited and, falling, to ignite the substance in the capsule.

Linings of Cup and Cover.—Both cup and cover are lined with platinum or gold-plated copper. The lining of the *cover* is sweated onto the steel. A platinum plug fitted into the vertical passage by which the gas enters serves to protect the steel surfaces of the valve seat and oxygen-channel from corrosion by the dilute nitric acid which condenses on the lining of the cover and which might otherwise be carried out into the channel when the valve is opened. The oxygen is admitted through the plug by a tubular passage, the outlet of which is horizontal, so that the current of gas may not blow directly upon the substance in the capsule.

The lining of the *cup* is made from a single sheet of metal which is spun to fit the steel cup accurately. It can be easily removed

from the latter by placing the fingers of the left hand inside the lining, and the thumb against the threads of the cup (which may be wrapped with cotton to protect the thumb), and drawing outward upon the lining, at the same time tapping the steel cup with a wooden mallet. The lining should be removed occasionally and any rust that may have formed on the inner surface of the steel polished off. Before the lining is put in again, the steel cup should be wiped out with a cloth moistened with oil.

For the lining, platinum has been used and has proved entirely satisfactory not only here but in other laboratories, but its high cost is an objection, and numerous attempts have been made to find a cheaper substitute. The Mahler bomb, which is in use in many laboratories, has a lining of enamel. So far as we are informed, it is found satisfactory save that it is apt to crack and scale off. We have found that aluminum linings, spun from the purest metal we can obtain, are attacked by the nitric acid to such an extent as to interfere with the accuracy of the determinations. Attempts to electroplate the inside surface of a steel cup with platinum or gold have been made by Berthelot[1] and also by Professor H. W. Wiley, chief of the Bureau of Chemistry, U. S. Department of Agriculture, but the results have been unsatisfactory, the lining either having proved porous and thus permeable to the oxygen and nitric acid, or having blistered, probably on account of the unequal expansion of the steel and the plating.

The most satisfactory substitute we have found for the platinum lining is one of copper heavily electroplated with gold. A cup was spun for us by the Middletown (Conn.) Silver Company from No. 20 Brown & Sharp gauge (0.8 mm.) sheet copper and electroplated by the International Silver Company of Meriden, Conn. A light plating of silver, two of gold of about 1 dwt. (1.5 grams) each, and finally three of gold of about 2 dwts. (3 grams) each were applied, each plating being thoroughly burnished before the next was deposited. This lining was used for four months or more. It was only after some 300 combustions had been made in it that blisters formed in the gold plating in two places on the bottom of the cup, and not until after the 400th determination, that copper could be detected in the bomb rinsings (which always contain free nitric acid). The same lining was then replated with gold and was in good condition after use in over 500 additional

[1] *Ann. chim. Phys.*, (5), **23**, 161.

determinations, when it was destroyed by an accident. Other linings of this description are now in use in different laboratories and while, at present, any positive conclusion as to their durability would be premature, it seems probable that, at least with occasional replating, a copper lining might serve for several thousand determinations.

In devising this gold-plated copper lining we have profited, particularly as regards the necessity of burnishing repeatedly during the deposition of the gold, by the experience of Mr. Henry J. Williams, of Boston, who has constructed and patented a calorimeter having a spherical bomb of aluminum bronze, electroplated internally with gold and externally with nickel. Mr. Williams' apparatus appears to have many excellent features. Its cost is, however, much beyond that of even the platinum-lined apparatus here described.

We have planned to use gold-covered copper ("rolled plate") instead of platinum for the lining of the cover but have as yet no experience in its use.

We find it a very decided advantage to have the lining and especially that of the cup easily removable. The low cost of gold-plated copper makes it easy to have two linings, so that if one gives out, it can be easily removed and repaired while the other is used in its place.

Metal Capsules.—The sample for combustion is held in a frustum-shaped metal capsule which is supported in the bomb as shown in Fig. 2. We employ capsules of three sizes: the small size, which is 1 cm. deep, 1.4 cm. in diameter at the base, and 1.6 cm. in diameter at the top, is used in most cases; the medium size, 1.7 cm. deep, 1.5 cm. in diameter at the base, and 2.2 cm. in diameter at the top, is employed for the combustion of urine absorbed in cellulose absorption blocks; the large size, 2 cm. deep, 1.5 cm. in diameter at the base, and 2.5 cm. in diameter at the top, is used in the combustion of milk upon asbestos (see below).

Until recently we have used exclusively capsules of platinum of the two smaller sizes. Those of the smallest size with a thickness of 0.15 mm. weigh only about 2 grams. They serve the purpose but are too thin for durability. A thickness of 0.20 to 0.25 mm. would be preferable. Those of the larger, *i. e.*, medium size, with a thickness of 0.35 mm. and weighing 7 grams, we find very satisfactory for use with the cellulose blocks employed for determining

the heat of combustion of urine. As the platinum capsules are rather expensive, we have recently used capsules of nickel. They are spun from $^1/_{64}$ inch (0.4 mm.) sheet nickel by the Goodwin & Kintz Company of Winsted, Conn., cost but a few cents each, and have thus far proved very satisfactory. To prevent their cracking, they are annealed and hammered and are so shaped that the sides join the base with a curve instead of a sharp angle. Before using, they are heated in the Bunsen flame until the surface is oxidized. When so treated, they withstand further oxidation for a considerable time even at the high temperature attained in the bomb.

Iron Wire.—The ignition of the sample in the bomb is brought about by means of a small coil of iron wire heated to ignition by an electric current. A spool containing about 25 grams of 0.007-inch (0.18 mm.) wire is furnished with each apparatus. This quantity, if cut into lengths of 2.5 inches (6.3 cm.) will suffice for about 2,000 combustions. By use of a simple "wire-measure," devised by Mr. Osterberg of this laboratory, a large number of wires of equal length may be prepared at one time. This measure consists of a cylindrical piece of hard wood, 2 cm. or more in diameter, having a longitudinal groove 0.6 cm. wide and 1 to 1.5 cm. deep. The cylinder may be conveniently prolonged into a handle. The wire is wound about this measure in as many turns as desired. By inserting one blade of a pair of shears into the groove, all the turns are easily cut at once. The pieces of wire, so cut, are made into coils by winding upon a pin or needle, leaving a half-inch of straight wire on each end. If the aggregate weight of the first ten pieces cut at one time is the same as that of the last ten of the same lot, the average weight of the twenty may be assumed to represent the weight of each piece of the lot.

Thermometer.—The thermometer used in determinations of heats of combustion must be capable of measuring small differences of temperature with as high a degree of accuracy as possible, since the chief source of error in the determination lies in these measurements, as explained below. At the same time, if the calorimeter is to be used in an ordinary laboratory room, the thermometer must be one that can be used over a considerable range of actual temperature. In specific terms, it must be capable of making measurements of temperature differences of 2° to 3.5°, accurate to a few thousandths of a degree, at an initial temperature

of 12° and also at an initial temperature of 25° or even higher (the initial temperature of the calorimeter being 2° or 3° below the room temperature). The requisite accuracy and adaptability are combined in "metastatic" thermometers of the Beckmann type. We have used for the most part a thermometer of this type made by Fuess of Berlin-Steglitz. It has a large bulb about 5 cm. in length and 1 cm. in diameter and contains about 32 grams of mercury. The scale is 23 cm. in length, divided into 6°, graduated to hundredths and capable of being read to thousandths with the aid of a lens. We have also used the Beckmann thermometer manufactured by Goetze of Leipzig.

With thermometers of this type, in addition to the ordinary correction for variations in the bore of the capillary, a second correction is evidently necessary for the reduction of the degrees of the scale to true centigrade degrees, for it is obvious that when the thermometer is set for use at a low temperature, the quantity of mercury in the bulb will be greater and the expansion per true degree, therefore, greater than when it is set for a higher temperature. Our Fuess thermometers have been calibrated by the Physikalisch-technische Reichsanstalt. By interpolating between the data of the certificate furnished by the Reichsanstalt we construct tables giving the caliber correction for each 0.1° and the "correction for setting" for each degree. For use in the laboratory, these tables can be most conveniently mounted on cards. Since the correction for setting is most conveniently used in a form different from that given in the certificate, we think it worth while to illustrate how the one is derived from the other.

The certificate accompanying one of our thermometers states that when the thermometer is set at 0° and heated to 6° (with the mean temperature of the projecting thread of mercury at 15°), 1° of the scale is found equivalent to 0.991° C.; when the thermometer is set at 25° and heated to 31° (projecting thread, 22°), 1° of the scale is equivalent to 1.002° C.; and when the thermometer is set at 50° and heated to 56° (projecting thread, 26°), 1° of the scale is equivalent to 1.013° C. The correction for 1° rise on the arbitrary scale is, therefore, —0.009° when the zero of the thermometer corresponds to 0° C. and +0.002° when it corresponds to 25° C., and since the change of the correction between 0° and 25° is the same as between 25° and 50°, *viz.*, +0.011°, we are justified in assuming that the change for each degree amounts

to 0.011° ÷ 25 = 0.00044°. For any setting of the thermometer between 0° and 50°, therefore, the correction to be applied for each degree of observed rise of temperature is $-0.009° + 0.00044n°$ where n = the true temperature to which the zero of the thermometer corresponds. The values of this correction for each degree are calculated to the nearest ten-thousandth of a degree and entered in the table of corrections. We determine the corrections for the Goetze thermometer by comparison with a Fuess which has been calibrated as above described.

For the reason that there is some danger of breaking thermometers of this type by improper handling, particularly in the case of the Fuess thermometer with its very heavy bulb, we give, for the benefit of the inexperienced, the following directions for changing the setting:

To set a thermometer of the Beckmann type for use at a temperature higher than that at which it has last been used, the bulb is warmed in the hand or in water until the mercury fills the whole of the capillary tube and a part of the upper reservoir. A portion of the mercury is then shaken off into the upper reservoir. This separation of the mercury may be effected by holding the thermometer vertically in one hand and either (1) tapping the outer tube ("envelope") near the reservoir smartly but not violently with the fingers of the other hand; or (2) striking the hand which holds the thermometer vertically against the other hand. Of the two methods, the former will usually separate a smaller portion of mercury than the latter. The thermometer should never be held in a horizontal or oblique position when jarred in either of these ways, as the inertia of so large a mass of mercury may produce so severe a transverse strain in the glass envelope as to break it.

To set the thermometer at a *lower* temperature, the mercury contained in the upper reservoir is brought into the upper part of the reservoir by inverting the thermometer and tapping the brass knob at the top gently on the table. The mercury will remain in the upper part of the reservoir when the thermometer is reinverted, *i. e.*, brought into normal vertical position with the bulb downward. The bulb is then warmed until the mercury in the capillary tube has joined that in the upper reservoir, then cooled until more or less of the mercury originally in the reservoir has been drawn into the capillary tube. The mercury remaining in the top of the reservoir is now separated and brought to the bottom by one of

the methods described above. With practice, the shifting of the mercury from capillary tube to reservoir, or *vice versa,* is easily and quickly accomplished.

Lens and Tapper for Thermometer.—The use of a lens to mag-

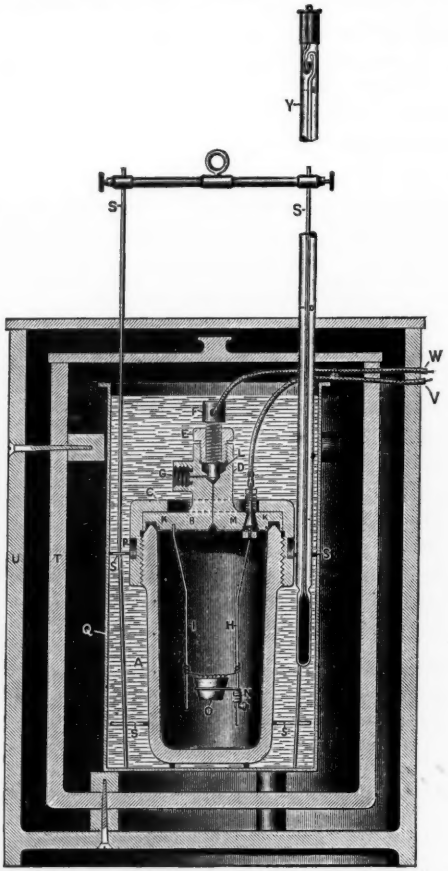

Fig. 4.—Bomb-calorimeter; apparatus as used for actual determinations of heats of combustion.

nify the divisions of the thermometer scale is essential. A Coddington lens of 1 inch (25 mm.) focal length (magnification = 10), made and mounted by the Bausch & Lomb Optical Co., Rochester, N. Y., has proved very satisfactory for this purpose.

For the prevention of errors of parallax, it is provided with an eye-hole and with a grooved adapter which fits against the envelope of the thermometer and serves to keep the principal axis of the lens at right angles to the thermometer scale.

To prevent lagging of the mercury in the capillary, the thermometer should be tapped on the brass cap, rather than on the glass envelope. A most useful and convenient tapper for this purpose is the hammer of a small electric bell which can be operated by a battery of two dry cells.[1] By means of a conveniently placed switch, the observer sets the hammer in motion a few seconds before each reading and stops it again after the reading is taken.

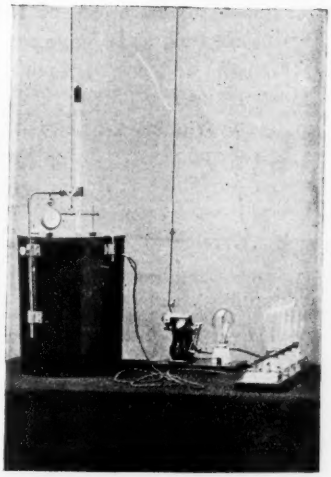

Fig. 5.—Bomb-calorimeter ready for a combustion.

Apparatus Mounted for Use.—The bomb, when ready for a combustion, is immersed in water contained in a metal cylinder. This cylinder is surrounded by concentric cylinders or pails of "indurated fiber," leaving air spaces to prevent undue passage of heat between the water and the outer air. The arrangement is shown in cross-section in Fig. 4 and, as it appears during a combustion, in Fig. 5.

[1] Such a tapper for a Beckmann thermometer was employed by Loomis (*Physical Review*, **1**, 206 (1894)) and also by Orndorff and Cameron (*Am. Chem. J.*, **17**, 517 (1895)).

Calorimeter Cylinder and Stirrer.—The cylinder is of britannia-metal 13 cm. in diameter, 23 cm. high, and holds, with the bomb, not far from 2 liters of water. A stirrer (SS), moved by a small motor or other agency, keeps the water in motion and insures the mixing needed for equalizing its temperature. This stirrer consists of two perforated annular pieces of sheet-brass connected by two brass rods which project out of the calorimeter and are there attached by thumb-screws to a nickel-plated cross-piece. A groove is cut in one side of the annular brass pieces to admit the thermometer. The calorimeter cylinder stands on cork supports which prevent it from coming in contact with the bottom of the pail. The interior of the britannia-metal cylinder should be kept clean and free from sediment.

The Outer Cylinders.—The diameters of the indurated fiber pails (U and T, Fig. 4) are such as to leave an air space of about 1 cm. between the two pails and one of 3 cm. between the inner pail and the calorimeter cylinder. The covers of the pails are of hard rubber. They are provided with holes for the two rods of the stirrer and for the thermometer. An adjustable standard attached to the outer pail (Fig. 5) bears an arm provided with a clamp for the support of the thermometer (Y, Fig. 4). On the arm is a hook upon which a watch may be conveniently hung near the thermometer. A second standard, with arm for support of the electric hammer for tapping the thermometer, may be adjustably attached to the main standard by a thumb-screw clamp. The current for igniting the iron wire over the substance to be burned in the capsule (O, Fig. 4) is conveyed by the rubber-covered wires (V, W), of which one is connected with the valve-screw of the bomb and the other with the insulated platinum wire (H) which passes through the cover.

Accessory Apparatus.

Apparatus for Moving Stirrer and for Igniting the Charge for Combustion.—The most convenient source of power for operating the stirrer we have found to be the direct or alternating current of the city electrical circuit, with suitable motors of about 1/20 horse-power. The same current serves to ignite the charge. As yet, no perfectly satisfactory substitute for these currents has been found. Six cells of the Edison-Lalande batteries have most nearly filled the requirements.

By means of a worm gear fastened directly to the armature

shaft of the motor, the speed is reduced, a final regulation being made, if necessary, by a rheostat, until the speed is such as to cause the stirrer to rise and fall about forty to fifty times per minute. With the apparatus as here described, it is important that the rate of stirring should not be less than 40 strokes (revolutions) to the minute. The connection between the motor and the stirrer is effected by means of a cord which is connected with the motor crank, passes upward to the ceiling or a shelf, over two pulleys, and thence down to the stirrer.

To heat the fine iron wire to incandescence, and thereby ignite the substance, requires a current of 3 or 4 amperes. If a 110-volt current is available, the necessary current may be obtained by switching it through four 32-candle power, 110-volt lamps in parallel. In case a 55-volt current is used, the 110-volt 32-candle power lamps would be replaced by a similar number of 16-candle power, 55-volt lamps. Lamps are especially desirable as resist-

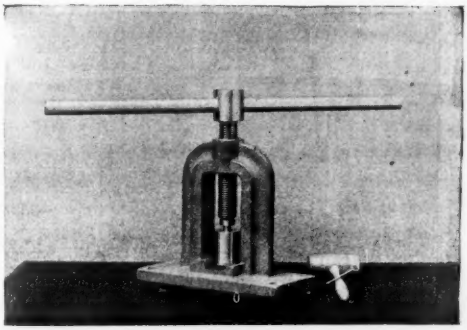

Fig. 6.—Pellet press.

ances since they indicate to the observer whether the circuit is actually completed by the closing of the switch and whether it is broken by the fusion of the iron wire.

Pellet Press and Mould.—Solid materials to be burned are usually pressed into small pellets, so that they may easily be held in the small platinum capsule within the bomb. This pellet form is advantageous, also, in preventing the mechanical losses of loose material, which might occur either before or after ignition, and so insuring the complete combustion of all the material. The mold resembles an ordinary "diamond mortar". The press (Fig. 6) is

so constructed that a pressure of 50 pounds (22.5 kilos), applied at the extremities of the screw arm, gives a pressure of over 10 tons (9,100 kilos) on the pellet pin. In practice, such a pressure is rarely needed.

In molding a pellet, care should be taken to adjust the mold exactly under the screw of the press before turning the latter down and not to exert so great a pressure on the screw as to distort the pin and cause it to stick in the block. A little oil should be used between the end of the screw and the top of the pin, and both block and pin should be kept clean and free from grit. To remove the pellet, the screw is slackened, the mold slid out and inverted and the head of the pin pressed against the table. If the

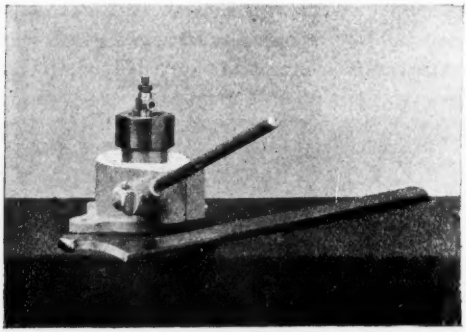

Fig. 7.—Clamp and spanner.

pellet cannot be removed in this way, the mold may be placed again under the screw of the press with the projection at the base *at right angles* to the groove of the press. By turning down the screw, the steel disk can be made to drop into the groove and can be easily pushed aside so that the pellet can be forced out in the same way. With a few substances (especially cane-sugar) it is necessary to wash and dry the mold after making each pellet, as otherwise some of the finely powdered substance may adhere to the inner surface of the mold and make the pin stick. The press screw is closely fitted and care must be taken not to injure it by turning it down its full length with any force, as might be done, for instance, by setting it rotating rapidly when the mold is not in place.

Clamp and Spanner.—To hold the bomb securely, while the collar is being screwed down, a clamp or vise (Fig. 7) has been

devised, consisting of a fixed and a movable jaw enclosing a nearly cylindrical but slightly tapering space for the reception of the cup of the bomb. The jaws are drawn together through a maximum distance of about 0.5 cm. by a lever with a very coarse half-thread. A paper lining in the clamp will prevent the cup's slipping, and protect it from being marred. The spanner is about 1 meter in length and is provided with a steel pin of about 1 cm. diameter, which fits into a hole in the bomb collar. In using the spanner,

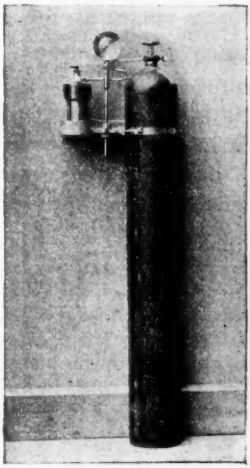

Fig. 8.—Appliances for filling the bomb.

care should be taken to fit the pin down its full length into the hole in the bomb collar; otherwise the edges of the hole may be worn away.

Bomb Support, Manometer, and Couplings for Filling Bomb with Oxygen from Oxygen Holder.—The oxygen used in this laboratory is furnished by the S. S. White Dental Mfg. Co., of Philadelphia, in cylinders about 125 cm. long and 18 cm. in diameter. These cylinders contain about 8 lbs., 8 oz., or 3850 grams oxygen, a quantity which should suffice for over 250 determinations. Brass coupling tubes are used to connect the cylinder with the manometer and with the bomb, which is supported, during the filling, upon a cast-iron shelf, as shown in Fig. 8.

The graduations of the manometer enable one to ascertain when

the supply of oxygen is nearly exhausted. When the pressure falls to 35 or 40 atmospheres, another cylinder of gas is ordered.

General Test of the Apparatus.

The general condition of the apparatus should be tested from time to time by check combustions. Benzoic acid and cane-sugar are convenient substances for this purpose, because they are easily obtained pure and their heats of combustion are accurately known (see p. 692). The benzoic acid has the advantage over the sugar that the pellets do not clog the pellet mold and that no kindler other than the iron wire is needed for the ignition.

II. METHOD OF USE OF THE APPARATUS.

Quantity of Substance To Be Used.

As explained below in the discussion of the accuracy of the method (p. 694), the quantity of material burned in the bomb should be such as will yield from 4000 to 7000 calories.

The following are suitable quantities of ordinary foods and feeding-stuffs:

Fats, oils, butter and very fat meats—as pork, fat mutton and fat beef	0.5 to 0.7 gram.
Leaner meats—as veal, fish, etc., and dried residue of milk	0.7 to 1.0 gram.
Vegetable products consisting mostly of starch, sugar, cellulose, etc., with more or less of proteids and not much fat—as sugar, starch, flour, meal, potatoes, fruits, seeds of cereals, legumes, etc., fodders and feeding-stuffs, including hay, straw, meals, etc	1 to 1.5 gram.

Of substances which we have found convenient for tests of the accuracy of the determinations, the following are suitable quantities:

Naphthalene and camphor	0.5 to 0.7 gram.
Benzoic acid and hippuric acid	0.7 to 1.0 gram.
Cane-sugar and glycocoll	1 to 2.0 gram.

Preparation of the Material for Combustion.

Solids.—Solids in general are powdered and pressed into cylindrical pellets in the pellet mold as described above. The material is weighed approximately before, and accurately after, molding. Food samples are used ordinarily in the "partially dried condition". The methods followed in this laboratory in preparing such samples have been previously described.[1] Fatty sub-

[1] Report of preliminary investigations on the metabolism of nitrogen and carbon in the human organism, by W. O. Atwater, C. D. Woods and F. G. Benedict. Bull. 44, U. S. Dept. Agr., Office of Experiment Stations, 1897.

stances, such as dried milk, are weighed directly into the capsule without molding.

With some substances, special devices are required to secure ignition. A crystal of naphthalene serves as a kindler for such substances as sugar and glycocoll. The naphthalene may be inserted between two turns of the coiled iron wire with one edge touching the substance in the capsule. Or, instead of a coil, the wire may be formed into a loop, resembling one of the forms of wire office clips used for holding sheets of paper together, and the naphthalene placed in the loop, which should touch the substance in the capsule.

Substances which are still more difficult to ignite, *e. g.*, creatin and creatinin, may be enclosed in gelatin capsules, such as are used with volatile liquids (see below).

Fats, such as butter, may be ignited with naphthalene, or, preferably, by use of a small quantity of fibrous asbestos, such as is used in Gooch crucibles. The asbestos is placed on the fat in such position that the burning iron wire may fall upon it. In this way too rapid cooling of the wire is prevented, and local ignition of the fat ensured.

Oils.—Oils are absorbed in fibrous asbestos. The metal capsule is half-filled with asbestos, ignited in a Bunsen flame, cooled in a desiccator and is weighed before and again after addition of the oil.

Volatile Liquids.—Volatile liquids, *e. g.*, alcohol, may be enclosed in gelatin capsules.[1] We have found the "Beekman ideal" capsule No. 00, which weighs from 0.11 to 0.19 gram, very convenient for the purpose.

Urine.—The heat of combustion of urine cannot be satisfactorily determined by simply burning the solid residue, because a portion of the organic matter after carbonizing becomes encased in the fused ash and is thus protected from oxidation.[2] We have met with the same difficulty in attempting to burn urine dried on asbestos fiber according to the method used for the combustion of milk (see below). The difficulty is obviated by absorbing and drying the urine in cylindrical blocks of cellulose as proposed by Kellner.[3] Suitable blocks are Carl Schleicher and Schüll's "No. 573" which are 15 mm. in height and 14 mm. in diameter and

[1] Berthelot uses collodion capsules for this purpose ("Traité pratique de calorimètrie chimique," p. 160).

[2] See Kellner: *Landw. Versuchst.*, **47**, 296 (1896).

[3] *Loc. cit.*

weigh about 0.7 gram. As the block and the dried urine are burned together, the quantity of heat due to the combustion of the cellulose must be estimated. It is scarcely practicable to determine once for all the specific heat of combustion[1] of the cellulose and to calculate from the weight of a block the heat that will be produced by its combustion, because the blocks contain varying quantities of moisture and are not easily dried to constant weight without danger of decomposition. If, however, a considerable number of blocks, say 50 or 100, are heated in the same drying oven at 95°-100° for three or four hours, they may then be assumed to have reached a uniform condition as to dryness and incipient decomposition. Determinations of the specific heats of combustion of three or four of the lot may, therefore, be made and the average result used for those burned with the urine. As the cellulose is very hygroscopic, the blocks should be kept in stoppered weighing bottles in desiccators over sulphuric acid and weighed in the same bottles. It is more convenient to have the weighing bottles large enough to hold several blocks.

The urine is prepared for combustion according to the following method, which was suggested by and is similar to that proposed by Tangl.[2] The weighed cellulose block is placed in an evaporating dish of 50 or 60 cc. capacity and the urine added from a 20 cc. pipette calibrated specially for urine.[3] One or two pipettefuls, *i. e.*, 20 or 40 cc., are taken according as the specific gravity is greater or less than 1.022. The weight of the urine is calculated from its specific gravity and the delivering capacity of the pipette. The urine is evaporated to dryness at 50°-60°. Repeated tests have shown that there is no appreciable loss of nitrogen in drying at this temperature. When dry, the block is transferred to the metal capsule and the urine residue remaining on the dish transferred to the capsule by wetting with water and wiping out with small quantities of fibrous asbestos held in bone-tipped forceps. After drying again at 50°-60°, the block is ready for combustion. The cellulose blocks will yield 2200-3000 calories each and the heat of combustion of urine ordinarily lies between 75 and 200 calories

[1] A convenient term for the heat of combustion per gram.

[2] *Arch. f. Physiol.*, Leipzig, 1869, Suppl. Bd., p. 251.

[3] A pipetteful of urine is delivered into a tared weighing-bottle and weighed. The quotient of the weight by the specific gravity gives a value for the delivering capacity of the pipette. A number of such determinations are made with urine of different specific gravities and the results averaged. The results obtained with the urines of different specific gravities, though agreeing substantially among themselves, differ materially from that obtained by calibrating with water.

per gram, that of urine of specific gravity 1.022 being in the neighborhood of 110 calories. The heat set free in the combustion will, accordingly, vary from 4400 calories ($110 \times 20 + 2200$) to 7400 calories ($110 \times 40 + 3000$), and at least 50 per cent. of this will come from the combustion of the urine.

For drying the urine it is desirable to have a self-regulating oven. An oven surrounded by a water-jacket, provided with a mercury thermostat, serves the purpose admirably. It will be found advantageous to provide a shelf in the oven with perforations into which the metal capsules may be set.

A serious difficulty in the determining of the heat of combustion of the unoxidized material of urine is the tendency to decomposition of urea and perhaps other compounds by which more or less of the potential energy is set free. We have found the danger of such loss of energy from urine on standing to be much greater than might be suspected, nor have we yet found a convenient way for preserving it for any considerable time with certainty that no loss occurs. We have been in the way of adding about 5 cc. of commercial formalin to 800 cc. of urine, keeping it in a refrigerator and making the combustion as soon as possible.

The drying of urine *in vacuo* at room temperature, as elaborated by Cronheim,[1] is probably the safest course. Preliminary experiments, made a number of years ago in this laboratory, but not published, indicated the success of the method but the length of time required renders its use extremely difficult when a large number of samples are to be prepared.

Milk.—For the combustion of milk, a metal capsule of the largest size is loosely filled with fibrous asbestos upon which the milk is then absorbed and dried. About 5 grams of milk should be used and care should, of course, be taken to secure a representative sample.

About 20 to 25 grams may be taken from the supply, after thorough mixing, and placed in a small stoppered flask or other weighing-bottle, from which the 5-gram portions for the individual combustions may be weighed out. The milk in the weighing-bottle should, of course, be mixed by shaking immediately before each portion is poured out.

Milk may also be dried and burned on the cellulose blocks used with urine, but the asbestos method described above has two ad-

[1] "Conservirung des Harns für analytische und calorimetrische Zwecke," *Arch. f. Anat. u. Physiol.*, Phys. Abth., Sup., 1902, p. 262.

vantages. The correction for the combustion of the cellulose is avoided and the number of weighings is decreased.

Filling the Bomb.

The bomb cover being supported upon a ring-stand, the capsule containing the pellet is placed in position in the platinum ring. The ends of the coil of iron wire are wound around the vertical platinum wires (one turn only) and the coil adjusted so that it touches the substance to be burned but not the capsule. The naphthalene (if any is to be used) is placed in position. The cover is now placed on the bomb and a little oil dropped upon the top to prevent its turning with the collar, which is then screwed on and tightened by means of the clamp and spanner. The bomb is now ready to be filled with oxygen. With its valve slightly open, it is placed in position on the iron shelf (see Fig. 8) and connected with the manometer which is kept permanently connected with the oxygen cylinder. The valve of the oxygen cylinder is then opened cautiously. When the manometer indicates a pressure of 20 atmospheres, the oxygen is cut off, the bomb-valve closed, and the bomb disconnected from the manometer.

Leakage of gas from the bomb may occur either at the soft metal gasket (K) or at the conical tip of the valve-screw (F) (Fig. 2). Gas escaping at the gasket will usually make an audible sound. If the gasket is not too much worn, the leak may be stopped by screwing the collar tighter. A leak at the valve can be easily and quickly detected by placing the moistened finger over the opening (G). When the valve-tip or the conical shoulder into which it fits becomes corroded so that the valve cannot be closed by gentle pressure, it must be reseated carefully in a lathe to secure a proper fit. If, in filling the bomb, leakage occurs at L (Fig. 2), the cylindrical screw (E) should be tightened a little to press the packing (L) tightly around the valve-screw.

Arranging Apparatus for the Combustion.

The calorimetric water should now be put in the britannia-metal cylinder. Both the quantity and the temperature of this water are to be regulated. In order to facilitate the calculations, it is better to make the quantity always the same and such that the total hydrothermal value of the calorimeter system will be a round number, such as 2000, 2100 or 2200 grams. (Our custom is to make it 2100 grams.) In order to reduce to a minimum the correction for

the influence of the surroundings upon the temperature of the system, the water in the cylinder should be made cooler than the surroundings of the system (as measured by an ordinary thermometer placed in the inner air-space) by about the expected rise in temperature, or a little more. For example, if the quantity of substance to be burned is such as will yield about 6300 calories and the hydrothermal value of the system is to be 2100 grams, the rise expected will be 3° and the water in the cylinder should be made 3°-3.2° cooler than the air of the inner air-space. The insertion of the bomb, which is at room temperature, will decrease this temperature difference by about one-sixth, the hydrothermal value of the bomb being about one-sixth that of the whole system, so that after the combustion the temperature of the system will be a little above that of the surroundings.

It is, obviously, more convenient to adjust the temperature of the water first and the quantity afterwards. The desired temperature can be readily obtained by mixing cooler water with that used in the preceding combustion (or with a portion of it). Water is then poured out of the cylinder until approximately the desired quantity remains; the cylinder, containing water and stirrer, is placed upon a tared balance, accurate to 1 gram, and small quantities of water are added or removed until the correct weight is obtained. The tare required is, of course, the desired hydrothermal value (*e. g.*, 2100 grams) minus the hydrothermal equivalent of the apparatus and plus the weight of the cylinder and stirrer.

The cylinder, containing stirrer and water, is now put in place inside the outer cylinders and the two conducting wires are joined, respectively, to the valve-screw and to the insulated conductor. The covers are put on and adjusted so that the stirrer will run smoothly, the thermometer is inserted and the stirrer set in motion. As soon as the different parts of the calorimeter system have assumed a common temperature, which usually requires two or three minutes, the mercury will begin to rise at a uniform rate, and the readings of the "initial" or precombustion period may begin.

The room temperature may have changed so much since the apparatus was last used that the thermometer must be reset. In that event, the water should be stirred a little after the insertion of the bomb and its temperature determined with an ordinary ther-

mometer, so that the actual temperature to which the zero of the reset thermometer corresponds may be known within half a degree.

Temperature Changes in the System.

If the calorimeter system were absolutely insulated thermally, only two temperature observations would be necessary for the determination of the heat of combustion of a substance. One of these could be made at any time after the system had come to internal temperature equilibrium after the insertion of the bomb and before the ignition of the substance, for the temperature would remain absolutely constant during this interval of time, whatever might be its length. This observation would give the *initial* temperature of the system. The second observation, that of the *final* temperature, could be made at any time after the heat from the combustion had distributed itself uniformly throughout the system, for then the temperature would again remain constant.

But it is, of course, impossible to insulate the system completely and, consequently, external influences are continually affecting its temperature. The most obvious and doubtless the most important of these external influences is the temperature of the medium surrounding the system. This medium may be regarded as made up of (1) the air of the inner air-jacket, (2) the walls of the inner indurated fiber cylinder, and (3) the air and walls of the outer air-jacket and the air of the room. Interchange of heat occurs between the system and (1) the air of the inner jacket by convection and radiation, (2) the indurated fiber cylinder by radiation, and (3) the air of the outer air-jacket and of the room by conduction through and convection by the rods of the stirrer. All of these interchanges may fairly be assumed to obey Newton's Law—that the rate of warming or cooling of a body is proportional to the difference of temperature between the body and the surrounding medium.

Less important external influences are (1) the production of heat by the friction and, in case of imperfect adjustment, by the impact of the stirrer, and (2) the evaporation of water from or condensation of water upon the system. The motion of the stirrer being regular, the quantity of heat produced by friction and impact (which is of course very small) is the same for any one minute as for any other. The amount of water condensed or evaporated during an experiment is without doubt very small in any case. At the same time it must be remembered that the latent heat of water

vapor at 20° being about 600 calories per gram, 1 calorie of heat is withdrawn from the system (and rendered latent) for every 0.0017 gram water evaporated. Conversely, the condensation of 0.0017 gram water upon the system would impart 1 calorie to it. Now, *condensation* can not occur at all except when the air of the inner air-space is so nearly saturated with moisture that its dew-point lies within 3° of its actual temperature, because the initial temperature of the calorimeter system is never more than 3° lower than the temperature of the surrounding air. The air of the inner air-space is practically completely enclosed by the inner fiber cylinder with its cover, so that very little air will diffuse in or out. Its volume is about 5.11 liters. This quantity of air, if saturated with moisture, would contain:

At 23° C	0.0204×5.11 gram.[1]
At 20° C	0.0171×5.11 gram.
Difference	$0.0033 \times 5.11 = 0.017$ gram.
Heat of vaporization	$0.017 \times 600 = 10$ calories.
At 30° C	0.0300×5.11
At 27° C	0.0255×5.11
Difference	$0.0045 \times 5.11 = 0.023$ gram.
Heat of vaporization	$0.023 \times 600 = 14$ calories.

If the initial temperature of the calorimeter were 27° (which is as high as it would be necessary to make it on a warm day in summer) and the air of the room (at 30°) were completely saturated with moisture, the quantity of heat imparted to the calorimeter by the condensation of all the moisture, from the air of the inner jacket would be 14 calories. In winter the initial temperature of the system does not exceed 20°, therefore the quantity of heat imparted to the system by condensation of moisture cannot be more than 10 calories. Moreover, even in the extreme cases now under consideration, the heat imparted to the system *during the experiment proper* will be very much less than the quantities mentioned, because the experiment proper is preceded by a "settling period" of at least two or three minutes and an "initial period" of five minutes, during which time the greater part of the moisture of the air will have been deposited and the dew-point will have fallen in consequence, so that the temperature of the system will have little more than begun to rise on account of the combustion of the substance in the bomb when it passes the dew-point of the air and

[1] See Smithsonian Phys. Tables, 2d ed., Washington, 1903, p. 155.

the deposition of moisture ceases. When we consider, further, how rarely the difference between the temperature of the air of a room and the dew-point will be as small as 3°, it is clear that the danger of error arising from the condensation of moisture upon the surface of the calorimeter system is insignificant.[1]

Evaporation of water, involving abstraction of heat from the calorimeter system, will occur much more commonly. This will be a slower process than that of dew-deposition and it seems probable that the 5.11 liters of air in the inner air-jacket will not become saturated with moisture in the length of time required for a determination, and it may safely be assumed that the difference in the amount of evaporation per minute will not vary materially in the course of the fifteen or twenty minutes required for the completion of the observations necessary for the determination of a heat of combustion.

The correction for the "external influences" may, therefore, be estimated on the assumption that the rate of warming or cooling of the calorimeter system in a given minute is proportional to the difference between the average temperature of the system for that minute and the temperature of the surrounding medium. Further, the temperature of the surrounding medium may be regarded as constant. The correction for the effect of external influences on the temperature of the system may, therefore, properly be determined according to the method of Regnault, which is based upon the assumptions just mentioned. This consists in estimating the effect produced on the temperature of the system by the external influences during each minute of the time intervening between the ignition of the substance and the reattainment of internal temperature-equilibrium after the combustion ("main" or "combustion" period of the determination) from determinations of the mean

[1] It ought, perhaps, to be pointed out that this conclusion refers only to this particular form of apparatus. In calorimeters having no covers to separate the air of the air-spaces from that of the room, especially where by means of a water-jacket the temperature of the air-spaces is regulated so as to be always the same (whatever the temperature of the room), the question of dew formation may be of greater importance. Stohmann, when using his constant pressure calorimeter (in which, of course, the rise of temperature being more gradual than in a bomb calorimeter, the time during which dew deposition may occur is greater), endeavored to keep the temperature of the air-spaces constant between 17° and 18° and made the initial temperature of the system always about 16°. As the temperature was frequently lower than the dew-point of the atmosphere in summer, long interruptions of work were sometimes necessary in that season of the year (*J. prakt. Chem.*, **143**, 22 (1887)). In his description of the method of use of the bomb-calorimeter, Stohmann again refers to the danger of dew formation and recommends that the difference between the initial temperature of the system and that of the surrounding air be not made too great (*J. prakt. Chem.*, **147**, 519 (1889)).

temperature of the system during each minute of this period and of the mean temperature and the rate of change of temperature during two periods of five minutes each, one (the "initial" period) immediately preceding, the other (the "final" period) immediately following the main period. The correction is most readily calculated from the actual observations of the temperature of the system, made at the beginning and end of the initial and final periods and at intervals of one minute throughout the main period by means of the formula derived by Pfaundler (see p. 688).

The Thermometer Readings.—Readings may be begun at any time after the stirrer has been set in motion. They should be continued until there has been a *uniform* rise of temperature for five minutes, the differences between successive readings not varying by more than 0.002°. These five minutes constitute the initial or precombustion period.

Precisely at the end of the five minutes (*i. e.*, at the sixth reading of the initial period), the electric circuit through the fine iron wire in the bomb is completed by closing a switch. The resistance lamps are incandescent during the passage of the current and the extinction of their light indicates that the iron wire has been fused. This usually occurs within two or three seconds after the closing of the circuit. The switch should now be opened immediately to avoid error from the production of heat in the calorimeter by the passing of the current through the water.

Readings should be continued at intervals of one minute until the rate of fall of the mercury has become regular—an indication that internal equilibrium has been regained. This marks the end of the combustion period. In our routine work, however, we find it convenient, for the sake of uniformity in the calculations, to regard the combustion period as ending, in all cases, five minutes after the ignition. With an apparatus of the present model, it may safely be assumed that the system will return to equilibrium within five minutes, if the rate of stirring exceeds 40 revolutions per minute. After the final reading of the combustion period, the stirring is continued for five minutes (final or "post-combustion" period), at the end of which time another reading is taken.

Before each reading, the thermometer should be tapped with the electric hammer.

After the Combustion.

The bomb is now removed from the calorimeter and placed in

the clamp. After the pressure has been relieved by opening the valve, the collar is unscrewed and the cover removed. The interior of the bomb and the lining of the cover are rinsed with water and the rinsings titrated to determine the nitric acid (see below). The quantity of iron, if any, remaining unoxidized must be deducted from the quantity originally taken. It may be determined by weighing or (more conveniently) by measuring its length on a millimeter or other finely graduated scale.

Determination of the Nitric Acid.

The temperature in the interior of the bomb during the combustion is so great as to bring about the combustion of some of the atmospheric nitrogen left in the bomb on filling and also of some of the nitrogen contained in the substance burned. The product of this combustion is nitric acid. The heat produced by the combustion of the nitrogen is, of course, to be deducted from the total heat measured. For the determination of the nitric acid we follow Stohmann in using a solution of normal sodium carbonate (Na_2CO_3) of 3.706 grams per liter. One cc. of this solution contains 0.003706 gram sodium carbonate which is equivalent to 0.004406 gram nitric acid, the heat of formation of which is 1 calorie.[1] Thus each cubic centimeter of sodium carbonate used in the titration represents 1 calorie set free in the calorimeter by the combustion of nitrogen. Methyl orange is used as indicator.

Calculation of Results.

To find the heat of combustion of the substance under investigation, it is necessary to determine the total quantity of heat liberated in the apparatus and to deduct from this total the quantities due to the "accessory combustions" of the kindlers and the nitrogen. To determine the total quantity of heat liberated, one must know (1) the hydrothermal value of the calorimeter system, and (2) the rise of temperature reduced to true degrees and corrected for the influence of the surroundings. The details of the calculation can be best explained by an example.

The following copy of a page of our laboratory book gives the observations made in a determination of the heat of combustion of cane-sugar with the calculations therefrom, arranged in the form we have found most convenient. At the top of the page are given

[1] Molecular heat of formation of nitric acid from nitrogen, oxygen and water equals 14,300 calories. Berthelot: *Ann. chim. phys.*, (5), **6**, 151 (1875); "Thermochimie," Vol. II, 107 (1897).

general data, such as the number and description of the sample, apparatus used, etc. Following this we have recorded the weighings of the sugar itself and of the iron wire and naphthalene and the titer of the nitric acid as found at the end of the determination.

SERIAL No. .....

Sample No.	Description, *Cane-sugar.*	Date, *July 13*, 1901.
Bomb No. *3.*	Observer, *J. F. Snell.*	Thermometer, No. *733.*

Capsule No. *1.*
Wt. caps. + subs. = *4.2501*
Wt. capsule = *2.8783*
Wt. substance, W = *1.3718*

CORRECTION FOR ACCESSORY COMBUSTIONS.
Wt. Fe *13.0* − *1.1* = *11.9* mgs. = *19.0* cal.
Wt. naphthalene = *6.4* " = *61.6* "
HNO_3 = *6.6* "
Correction for accessories = *87.2* "

INITIAL PERIOD.

READINGS.	CORRECTED READINGS.
1 *1.018*	*1.015*
2 *1.021*	
3 *1.025*	
4 *1.027*	
5 *1.030*	
$6\theta_0$ *1.032*	*1.029*

MAIN PERIOD.

$7\theta_1$ *2.300*	*2.3*
$8\theta_2$ *3.650*	*3.7*
$9\theta_3$ *3.678*	*3.7*
$10\theta_4$ *3.662*	*3.7*
$11\theta_5$ *3.653*	

FINAL PERIOD.

$\frac{\theta_5 + \theta_0}{2}$ =	*2.3*
Sum =	*15.7*
5θ =	*5.1*
Diff. =	*10.6*
Log. diff. =	*0253*
Log. V′−V =	*7324*
Colog $\theta'-\theta$ =	*5820*
	3397
Antilog. = +	*.0219*
+ 5 V = −	*.014*
Radiation correction = +	*.0079*
16 *3.640*	*3.633*

Time *3.30*

INITIAL PERIOD.
Fall = − *.014*
Rate V = − *.0028*
Mean t°, θ = *1.022*

CORRECTED READING, θ_5 = *3.646*
θ_0 = *1.029*
$\theta_5 + \theta_0$ = *4.675*
½ = *2.3*

FINAL PERIOD.
Fall = + *.013*
Rate V′ = + *.0026*
V = − *.0028*
V′ − V = + *.0054*
Mean t°, θ' = *3.640*
θ = *1.022*
$\theta'-\theta$ = *2.618*

THERMOMETER CORRECTION.
T° air = *25.2*
T° water = *23.8*
1st reading = *1.0*
T° of zero = *22.8*
Corr. for 1° = + *.001*
Rise (degrees) = *2.6*
Ther. corr. = + *.0026*

FINAL CALCULATION.
θ_5 = *3.646*
θ_0 = *1.029*
$\theta_5 - \theta_0$ = *2.617*
Th. corr. = + *.0026*
Rad. corr. = + *.0079*
Corr. rise = *2.6275*
" " × 2100 = *52.550*
= Total heat = *5517.8*
Accessories = *87.2*
Corrected heat = *5340.6*
Log. corr. heat = *73485*
Log. W = *13729*
59756
HEAT OF COMBUSTION PER GRAM = *3959*

Remarks:

Below the second horizontal line are given at the left of the page the thermometer readings. The last reading, No. 16, will be found near the foot of the page, below the calculation of the radiation correction. Corrections on account of variations in thermometer bore are applied to readings 1, 6, 11, and 16, and the corrected values given in the next column, with the exception of No. 11 $(\theta)_5$, which is placed for convenience in the third column and repeated in the fourth.

The total rise of the thermometer during the combustion period amounts to $3.646° - 1.029° = 2.617°$ of the arbitrary scale of the thermometer (see Column 4, "Final Calculation"). To this "apparent" rise of temperature, two corrections are to be applied:

(1) The degrees of the arbitrary thermometer scale are to be reduced to true degrees (thermometer correction).

(2) Allowance is to be made for the influence of the surroundings upon the temperature of the calorimeter during the combustion period (radiation correction).

Thermometer Correction (Column 4).—The temperature of the water at the beginning of the combustion was 23.8° C. The reading of the calorimeter-thermometer corresponding to this temperature is 1°. The zero of the thermometer corresponds, therefore, to 22.8° C. At this temperature, 1° of the arbitrary scale of the thermometer is equal to 1.0010 true degrees. A correction of + 0.001° is therefore to be made for each degree of apparent rise of temperature, or a total correction of $0.001 \times 2.6 = +0.0026°$.

Radiation Correction (Columns 1-3).—During the early part of the combustion period, the calorimeter, *i. e.*, the calorimeter system, is cooler than the surrounding air. The temperature is rising as the calorimeter system gains heat from the air. In the later part of the period, the calorimeter is ordinarily warmer than the air and its temperature is falling as heat passes from it to the air. According as the quantity of heat gained during the early part of the period is greater or less than the quantity lost later, the observed rise of temperature is greater or less than that properly attributable to the combustion and a subtractive or additive correction is to be made.

The correction is calculated by the Regnault-Pfaundler formula,[1]

$$C = nV + \frac{V' - V}{\theta' - \theta}\left(\frac{\theta_n + \theta_o}{2} + \sum_1^{n-1} \theta - n\theta\right),$$

[1] Pfaundler: Pogg. *Ann.*, **129**, 113 (1866).

where n = number of time units (minutes) in combustion period.

V = rate of fall of temperature of calorimeter during initial period.[1]

V′ = rate of fall of temperature of calorimeter during final period.[2]

θ = mean temperature of calorimeter during initial period.

θ' = mean temperature of calorimeter during final period.

$\theta_1, \theta_2 \ldots\ldots \theta_n$ = temperature at end of first, second, ... nth minutes of combustion period.

θ_o = temperature at moment of ignition.

Applying this formula to our example, we find for the expression within the bracket 10.6° (see first column); for V′—V, 0.0054°, for $\theta'-\theta$, 2.618° and for nV, $5\times(-0.0028) = -0.014°$ (see middle column); whence C = + 0.0079° (see first column).

Applying the thermometer and radiation corrections, we have $2.617 + 0.0026 + 0.0079 = 2.6275$ as the rise of temperature in true degrees (see "Final Calculation" in last column). The total hydrothermal value (water + hydrothermal equivalent of apparatus) being 2100 grams, the quantity of heat set free in the apparatus must have been $2.6275 \times 2100 = 5517.8$ calories.

Correction for Accessory Combustions.—The weight of the iron wire was 13 mg. The quantity unburned was 1.1 mg. The quantity burned was therefore 11.9 mg. The specific heat of combustion of iron being 1601 calories, the heat of combustion of 11.9 mg. is $11.9 \times 1.6 = 19$ calories. The quantity of naphthalene burned was 6.4 mg., which yields $6.4 \times 9.63 = 61.6$ calories, the specific heat of combustion of naphthalene being 9628 calories. The heat from the combustion of nitrogen as determined by titration of the nitric acid is 6.6 calories. The total heat from accessory combustions is therefore $19 + 61.6 + 6.6 = 87.2$ calories.

Deducting this quantity from the total heat set free in the apparatus, we have $5517.8 - 87.2 = 5430.6$ calories as the heat due to the combustion of the sugar. The quantity of sugar burned was 1.3718 grams. The specific heat of combustion according to this determination is therefore $5430.6 \div 1.3718 = 3959$ calories.

It will be found convenient to have tables mounted on cards,

[1] The change is actually a rise but for convenience in mathematical calculation it is here expressed as a fall in temperature. The value of V thus becomes negative.

[2] The change is generally a fall in temperature. Sometimes, however, the initial temperature of the water or the quantity of heat set free may be such that final temperature of the calorimeter will be lower than that of the surroundings, in which case there will be a rise of temperature and the value of V′ will be negative.

giving the heat of combustion of quantities of naphthalene weighing from 4 to 10 mg. and of quantities of iron weighing from 10 to 20 mg. The weights may be expressed to tenths of milligrams and the heat quantities to tenths of calories. If iron wire of uniform diameter is used, the quantities of iron may be more conveniently expressed in lengths instead of weights. The specific heat of combustion of naphthalene is 9628 calories and that of iron 1601 calories.

Heat Unit.

The unit in which the heat of combustion, as thus calculated, is expressed is the quantity of heat necessary to raise the temperature of 1 gram of water 1° at the temperature which the water has in the determination in question. (In the above example it ranges from 23.8° to 26.4°.) Since the variations in the specific heat of water between 15° and 30° are small,[1] it scarcely seems necessary to correct results obtained at any ordinary room temperature for the variation of the specific heat of water from its value at 15° or 20° C. No error of any consequence will be committed, for instance, by taking 3959 calories as the determined specific heat of combustion of cane-sugar, whether the calories be defined as the heat necessary to raise the temperature of 1 gram of water from 15°-16° or from 20°-21° C.

Reduction to Constant Pressure.

The heat of combustion determined in the bomb calorimeter is that at constant volume, while the heats of combustion customarily

[1] The following table gives the results of determinations of the specific heat of water at 15° and 30° by different experimenters and different methods. The specific heat at 20° is taken as unity.

SPECIFIC HEAT OF WATER AT 15° AND 30° REFERRED TO THAT AT 20°.

		Specific heat of water.		
				Difference.
Experimenter.	Method.	at 15°.	at 30°.	30–15°.
Bartoli and Stracciati[1]	Mixtures.	1.0005	1.0014	—0 0009
Ludin[2]..... ...	"	1.0009	0.9999	+0.0010
Rowland[3]	Frictional heating.	1.0014	0.9986	+0.0028
Griffiths[4]	Electrical heating.	1.0014	.....	.....
Callendar and Barnes[5].....	"	1 0010	0.9987	+0.0023

[1] Bartoli and Stracciati: *Estratti dal Nuovo Cimento*, Series 3, Vol. 32. (1891). We have derived the figures from a table by Pernet in Louguinine's *Bestimmung der Verbrennungswärme*, p. 18.

[2] Ludin: Inaugural Dissertation, Zurich, 1895. We have derived these figures also from Pernet's table.

[3] As corrected by Waidner and Mallory, *Phys. Review*, **8**, 232 (1899).

[4] Value corrected by F. A. Wolff, Johns Hopkins Univ. Circular, June, 1898, cited by Waidner and Mallory, *Loc. cit.*, p. 235.

[5] Callendar and Barnes: *Phys. Review*, **10**, 213 (1900).

tabulated and used are those at constant pressure. To reduce the molecular heat of combustion of a solid or liquid compound, $CnHpNrOq$, at constant volume to that at constant pressure, it is necessary to add $(\frac{1}{2}p - q - r)$ T calories where T = the absolute temperature of the calorimeter.[1] To reduce the *specific* heat of combustion at constant volume to that at constant pressure the term to be added is, therefore, $(\frac{1}{2}p - q - r)$ T ÷ M, where M = the molecular weight of the substance. For carbohydrates, this correcting term is zero, *i. e.*, the heats of combustion at constant volume and at constant pressure are identical. For tripalmitin it amounts to + 15.6 calories, for tristearin to + 16.1 calories, and for triolein to + 15.2 calories. For protein it amounts to about + 3 calories.

With food materials in general, therefore, the heats of combustion obtained by the bomb-calorimeter should be increased by 15-16 calories for each gram of fat and by 3 calories for each gram of protein.

III. DETERMINATION OF THE HYDROTHERMAL EQUIVALENT OF THE CALORIMETER.

Now that the heats of combustion of many compounds are accurately known, the most convenient and satisfactory method for the determination of the hydrothermal equivalent of a bomb-calorimeter is to burn weighed quantities of such compounds in the bomb immersed in a known quantity of water.[2] From the observed rise of temperature and the known heat of combustion of the compound used, the total water value of the calorimeter system is calculated. Deducting from this the quantity of water used, we have the water value of the calorimeter itself.

The substances used in these determinations should be such as can easily be obtained pure and preserved without risk of change by deliquescence, oxidation, decomposition or otherwise. Their heats of combustion should have been determined in calorimeters whose hydrothermal equivalents have been learned by other methods.[3] Those which have been determined by several investigators, independently and with closely accordant results, are to be preferred. Stohmann selected hippuric acid, benzoic acid, cane-

[1] See Berthelot: *Thermochimie*, **2**, 30 (1897).

[2] Stohmann: *J. prakt. Chem.*, **157**, 99 (1894).

[3] For descriptions of such methods see Stohmann, Kleber and Langbein: *J. prakt. Chem.*, **147**, 524 (1889); Berthelot: *Traité practique de calorimétrie chimique*, 144ff.; Wiley and Bigelow: This Journal, **19**, 439 (1897).

sugar and camphor as suitable for the purpose, these being substances for whose heats of combustion fairly accordant values had been obtained in his own laboratory and that of Berthelot. We have used substances of which we had specimens known to be pure from previous determinations of carbon, hydrogen and nitrogen and which were at the same time substances with regard to whose heat of combustion Stohmann and Berthelot were in approximate agreement. The substances happen to be the same as those recommended by Stohmann, except that we have used glycocoll instead of camphor.

Camphor, hippuric acid and benzoic acid are ignited directly by the heated iron wire but with cane-sugar and glycocoll a kindler (a naphthalene crystal) should be used.

The following are the specific heats of combustion of the five substances in question.

Stohmann used his own figures in preference to those of Berthelot. We have used the average.[1]

	Stohmann.	Berthelot.	Tower.[2]	Average.
Glycocoll	3129.1	3133.6	....	3131
Cane-sugar	3955.2	3961.7	3958.7	3959
Hippuric acid	5668.2	5659.3	....	5664
Benzoic acid	6322.3	6322.1	....	6322
Camphor	9291.6	9288.0	....	9290

In order to check the accuracy of the bomb, it is customary in this laboratory to make a combustion of cane-sugar about every two weeks. The average of the last twenty combustions thus made is 3959.3 calories per gram. The minimum result was 3948 and the maximum 3967.

If m be the number of grams of substance burned, q_1 the heat of combustion per gram, the quantity of heat liberated by the combustion will be mq_1 calories. If, at the same time, q_2 calories are produced by the accessory combustions of iron wire, of nitrogen and of kindling material (such as naphthalene), the total heat, q, set free within the calorimeter will be $q = mq_1 + q_2$; and if t be in degrees centigrade, the observed rise of temperature (corrected for thermometer calibration and for influence of surroundings of

[1] That Stohmann's methods of manipulation were more painstaking than Berthelot's is very plain to one who has seen both as actually carried out in their respective laboratories. At the same time, Stohmann's special refinements probably made but little difference in the actual results. W. O. A.

[2] Unpublished experiments made in this laboratory.

calorimeter), w the weight of water used, and a the required hydrothermal equivalent, evidently $q = (w + a)t$, whence

$$a = \frac{q}{t} - w.$$

The method of calculation is illustrated by the following example:

	Substance.	Quantity burned. Grams.	Specific heat of combustion. Calories.	Heat liberated by the combustion Calories.
	Cane-sugar	1.0177	3959	4029.0
Accessories	Iron	0.0201	1600	32.2
	Naphthalene	0.0078	9628	75.1
	Nitrogen (by titration of the nitric acid formed)			6.0
	Total heat liberated, q			4142.3
	Corrected rise of temperature, t.....			1.9751°
	Weight of water used in calorimeter, w			1685 g.

whence, $a = \frac{4142.3}{1.9751} - 1685 = 412$ grams.

A number of determinations (at least three) of a are made in this way with each of three or four substances. The triplicate results with each substance should agree very closely with each other as should the several averages of these triplicates. If the latter do not differ by more than a few (*e. g.*, 5) grams, the average of these averages may be taken as the correct hydrothermal equivalent of the calorimeter.

To insure that the hydrothermal equivalent thus obtained shall be actually that of the apparatus as used subsequently for determinations of heats of combustion, the quantity of water used in the calorimeter in the determinations of the hydrothermal equivalent should be as nearly as possible the same as in the regular determinations. In the above example, for instance, 1685 grams of water were used, because we knew that the hydrothermal equivalent was not far from 415 grams and it was our intention to have regularly a total water-value (water + hydrothermal equivalent) of 2100 grams.

A tolerably close estimate of the hydrothermal equivalent may be made in advance of the accurate determinations by calculation from the weights and specific heats of the *materials* of which the calorimeter is constructed, only those parts being taken into account which share the temperature rise of the water. These are,

of course, the water cylinder, the lower parts of the thermometer, the lower part of the stirrer, and the bomb with its contents. A statement of the weights of the component materials is furnished with each of the calorimeters here described. The following are the specific heats as nearly as we know them:

Material.	Sp. heat.	Source of figures.
Bomb:		
Tool steel	0.1087	Determined by Dr. Tower.
Hotchkiss gun steel	0.1114	" " "
Platinum	0.032	Smithsonian Phys. Tables, 2nd ed., Washington, 1903, p. 296.
Lead	0.030	Smithsonian Phys. Tables, 2nd ed., Washington, 1903, p. 296.
German silver	0.094	Tomlinson: Proc. Roy. Soc., 1885.
Oxygen (constant volume)	0.157	Wüllner, "Experimental Physik," (4th ed.), III, 509.
Water-cylinder:		
Britannia-metal: 90 pct. tin	0.054	Smithsonian Phys. Tables.
Britannia-metal: 7 pct. antimony	0.049	" " "
Britannia-metal: 3 pct. copper	0.092	" " "
Stirrer:		
Brass	0.094	Kohlrausch, Phys. Meas.
Thermometer:[1]		
Mercury	0.033	Smithsonian Phys. Tables.
Glass	0.19	Kohlrausch, Phys. Meas.

IV. ACCURACY OF THE METHOD.

Theoretical Discussion.

If m be the quantity of substance burned, $h = a + w$, the hydrothermal value of the calorimeter system, a being the hydrothermal equivalent of the apparatus and w the weight of the water, and t the rise of temperature of the system due to the combustion; then the specific heat of combustion of the substance, $q = \frac{ht}{m}$.

From this formula it is clear that errors making h or t too large or m too small will make q too large in the same proportion, and errors making h or t too small or m too large will make q too small in the same proportion. An error in a, the hydrothermal equivalent of the apparatus, will affect equally all determinations made with that apparatus, *i. e.*, will produce the same percentage error in each. Errors in m, w, or t, on the other hand, will affect only the individual determination.

[1] We have found by examination of a broken Fuess thermometer of the kind used in this laboratory and described above, that the portion immersed in the calorimeter water consists of about 8.5 grams glass and 32.5 grams mercury.

Allowing a possible error of ±0.0002 grams in weighing the substance, we have a possible error in m and therefore also in q of ±0.02 per cent. when 1 gram, or of ±0.04 per cent. when 0.5 gram is used. Allowing a possible error of ±1 gram in the weighing of the water, the possible error in h, leaving out of consideration the constant error in a, is ±0.05 per cent. on a hydrothermal value of 2100 grams. The possible error due to t will, however, be greater. ±0.001° must be allowed on each reading of the thermometer or ±0.002° on the two readings necessary to determine a temperature difference. In addition, the correction for the influence of the surroundings upon the temperature of the calorimeter is uncertain. If we allow another ±0.002° (which is probably a liberal estimate) for error here, we have a possible total error of ±0.004°. In the measurement of temperature differences of from 1° to 4°, the maximum errors, on the above assumption, will be from 0.4 to 0.1 per cent.

It is clear, then, that for accurate results the greatest care is needed in the temperature measurements. To secure this accuracy:

(1) The quantity of substance burned should, if practicable, be large enough to give a rise of from, say, 2° to 3.5°. In other words, if the water-value of the calorimeter be made 2100 grams, a quantity sufficient to yield 4000 to 7000 calories or a little more should be used.

(2) The thermometer must be accurate and must be accurately read and corrected.

(3) The temperature of the air-space immediately surrounding the metal cylinder should be kept constant throughout each experiment so that the conditions may be correct for the application of the Regnault-Pfaundler "radiation correction" (see above). So far as we are aware, the most accurate experimenters in this field work in rooms of constant temperature, and some protect their calorimeters from radiation from the observer's body by enclosing them in metal cylinders having double walls with interspaces filled with water. According to our experience, however, the two indurated fiber cylinders of our calorimeter afford sufficient protection, and reasonably accurate determinations may be made in an ordinary laboratory room, provided the temperature is nearly constant during each experiment. We have, however, arranged a small room in the center of the basement of our laboratory for this special work.

Accuracy of Actual Determinations.

In the actual use of the apparatus, the accuracy attained is about what would be expected from the foregoing considerations. Thus, in thirteen determinations of the heat of combustion of benzoic acid, made by three observers in this laboratory, the average deviation of the individual results from the mean was ±0.16 per cent. and the maximum deviation —0.35 per cent. The minimum quantity of substance burned being 0.8 gram, we should anticipate a possible error of ±0.03 per cent. in the weighing. The minimum rise of temperature produced in the calorimeter being 2.5°, we should look for a possible error of ±0.16 per cent. in the determination of the temperature difference. Allowing a possible error of ±0.05 per cent. in the weighing of the water and leaving out of consideration personal error and error due to the use of different apparatus, we should expect to find a maximum error of 0.03 + 0.16 + 0.05 = ±0.24 per cent. in the individual results. The actual maximum error was, as just stated, —0.35 per cent. The difference barely exceeds that between the specific heat of water at 15° and at 30° (see p. 690, foot-note).

That, in general, the actual determinations on solids and homogeneous liquids have very nearly theoretical accuracy is shown by the following comparison of anticipated errors, estimated in the manner just illustrated, with the actual deviations of the results of individual determinations from the average of those results.

Substance.	No. of determinations.	No. of samples.	No. of observers.	Maximum error. Anticipated. Per cent.	Maximum error. Actual. Per cent.	Mean error. Actual. Per cent.
1. Benzoic acid	13	..	3	±0.24	—0.35	±0.16
2. Hippuric acid	9	..	3	0.31	—0.39	0.22
3. Cane-sugar	18	..	4	0.38	+0.51	0.28
4. Cellulose blocks	15	5	3	0.38	+0.43	0.17
5. Commercial oils	84	40	1	0.29	+0.39	0.12
6. Beef	8	4	2	0.23	±0.20	0.07
7. Dried residues of milk	8	4	1	0.22	±0.14	0.11
8. Other foods of animal origin, *e. g.*, butter, pork, casein	10	5	2	0.29	±0.20	0.09
9. Vegetable foods and fodders, largely carbohydrate in composition	14	7	2	0.27	±0.18	0.10
10. Human feces	10	5	3	0.24	±0.25	0.12

This comparison indicates pretty clearly, we think, that with substances of these classes, there cannot be any very important sources of error other than those discussed above, also that the allowance of $\pm 0.002°$ for uncertainty in the radiation correction is ample.

From the table, it would appear that the determinations on substances of mixed composition were actually more accurate than those on pure chemical compounds. The explanation of this is, doubtless, partly that in the case of the substances of mixed composition, the quantities burned were such as to set free larger quantities of heat, thus reducing the anticipated maximum error, and partly that on these substances the duplicate or triplicate determinations on each sample were made by a single observer with a single apparatus, while the determinations on benzoic acid, hippuric acid, cane-sugar, etc., were made by more than one observer with more than one apparatus.

With a substance of uniform composition, combustible without the aid of a kindler, it is a safe practical rule, in case only two determinations are ordinarily made, to make an additional determination whenever the duplicates vary from each other by 0.5 per cent. or more (*i. e.*, from their average by ± 0.25 per cent. or more) and in case three or more determinations are made, to reject results varying from the average by over ± 0.4 per cent.

Where a kindling substance is used, especially when, as in the combustion of urine on cellulose blocks, the kindler furnishes a considerable proportion of the total heat measured, greater latitude between duplicates must be allowed and lower accuracy of result accepted. If 20 cc. of urine (a little over 20 grams), having a specific heat of combustion of 110 calories, be burned with a cellulose block yielding 2200 calories, the maximum error anticipated will be ± 0.4 per cent. in the determination of the temperature difference and about ± 0.2 per cent. due to the use of the kindler, or about ± 0.6 per cent. in all. Duplicates varying by less than 1.2 per cent. should, therefore, not be rejected, but an additional determination should be made in case the duplicates differ by over 0.5 per cent.

With milk, owing to the great difficulty of taking uniform samples, the variations between duplicates sometimes amount to 2 per cent. or more. Where such wide differences occur, a third determination is obviously necessary, but until a better method of

sampling milk is devised, we must be content to accept less accurate results with this substance than we are able to obtain with solids and with liquids of uniform composition.

Verification by the Respiration Calorimeter.

Experimenters with the bomb-calorimeter have felt the lack of an absolute standard for verification of the accuracy of the results obtained by its use. Such a verification is found in comparative measurements of the heat of combustion of alcohol by the bomb-calorimeter and by the Atwater-Rosa respiration calorimeter[1] in this laboratory.

To establish the accuracy of this latter apparatus as a calorimeter, known amounts of heat are introduced electrically, and are measured by the apparatus. In the average of a large number of determinations, the disparity between the amounts introduced and the amounts as measured has been about 1 part in 10,000.

The accuracy of the apparatus for the determination of heat being thus shown, considerable quantities of alcohol are burned in the respiration chamber during long periods (about 40 grams per hour during periods of twelve to one hundred hours each) and the heat thus produced is measured and the heat of combustion per gram of alcohol is determined. Aside from the possibility of a slight error in the figure 0.592, which was employed for the latent heat of evaporation of water, it seems hardly probable that there can be any considerable error in the average of the results obtained. Omitting from consideration the experiments in which obvious disturbing factors influenced the results, and considering only the experiments of the past three years, during which earlier errors of various kinds were eliminated, eleven series of experiments performed during the years 1900-2 gave figures for the heat of combustion of alcohol which averaged 7090 calories per gram. The maximum and minimum figures were 7111 and 7048 respectively, the range of error being thus ± 0.6 per cent. The average of six determinations with the bomb-calorimeter, corrected for constant pressure, was 7.095 calories, the maximum and minimum being 7110 and 7068 respectively, and the range of error ± 0.4. In other words, the average of the determinations with the bomb differs from that with the respiration calorimeter by only 0.07 per cent.

[1] U. S. Dept. Agr., Office of Experiment Stations, Bulletins 63, 69 and 109.

We thus have a standard to which the determinations by the bomb-calorimeter are referable and which shows them to be correct.

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PETROLEUM IN CALIFORNIA.

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WITHIN the last few years California has developed a new industry, that of petroleum. The knowledge that it existed is not new. Seepages occur in various parts of the State, and natural gas is found over a very large area. Immense deposits of asphaltum occur in the southern counties and were used by the early Mission Fathers. Attempts were made to distil the crude oil and in 1855, Pico erected a small refinery.

The discovery of oil in Pennsylvania produced great excitement, not only in the east but in California. Claims were located in all parts of the State and companies formed to work them. In 1865 there were sixty-five companies in existence with a nominal capital of $45,000,000. Oil properties were exploited in every county from Humboldt to San Diego, but there was no apparent success, owing to lack of prospecting, insufficient depth of wells, and to the opinion of eminent chemists and geologists that the oil would not be found in large quantities, and could not be refined.

Petroleum occurs in every part of the State, but as yet only the southern part yields any large quantity. Ventura, Los Angeles, Orange, Santa Barbara, Kern and Fresno Counties furnish practically all the oil that is produced, although in many other counties small yields have been obtained.

Los Angeles, in common with other districts, was exploited nearly forty years ago, but no oil was obtained. The wells were not bored deep enough. Nothing further was done for thirty years, until in 1892 a well 365 feet deep was sunk and yielded oil. In three years, more than 300 wells were drilled and most of them yielded oil. Other districts in the neighborhood were exploited, and hundreds of new wells located. The production of oil rapidly increased until in 1897 it had reached 1,400,000 barrels. The total amount of oil obtained from the Los Angeles district amounts to more than 9,000,000 barrels. About 1400 wells have been dug,

none of them very deep. The oil sand averages about 60 feet in thickness. A second sand has been worked with profit, and it is believed that a third sand exists.

Other districts in Los Angeles County have been worked for oil, the principal ones being Whittier, Fullerton and Puento. This oil is usually light in gravity, so much so that the most of it is distilled and only the residuum used for fuel. In Ventura County there are more than 500 wells, over 300 of them being worked now; they are from 500 to 2000 feet deep. Practically all are owned by the Union Oil Company. In Santa Barbara County, oil seepages have long been known. In 1895 some wells were dug on the beach at Summerland, and oil was struck at the depth of only 125 feet. The deepest are only about 400 feet. Since then more than 300 wells have been bored, some on the beach and some on the ocean, 400 to 1200 feet from the shore. Some of the wells in other districts are 1000 or more feet deep. The oil is heavy, averaging about 14° Bé. The yield is between 8000 and 10,000 barrels a month but has been much more. The Fullerton and Brea districts in Orange County produced last year over 1,000,000 barrels. The oil varies greatly in gravity, from heavy, 14° Bé., to as light as 35° Bé.

North of the Tehachapi, the whole valley of the San Joaquin seems to be underlaid with oil, although as yet only a small area is worked. The principal fields are in Fresno and Kern counties. In Fresno County is the well-known Coalinga district. This field is limited in extent, extending over but a few sections, but in this area there are very many wells. Some are very deep, one being 2300 feet. The oil is of different qualities, some very heavy and black in color, others very much lighter, about 35° Bé. There are two pipe lines to transport the oil to the railroad, and a pipe line to the ocean is about to be commenced.

Another district in Fresno that has produced some oil is Kreyenhagen, 22 miles southeast of Coalinga. Like Coalinga, it produces two qualities: one green and light, 35° Bé., and one black and heavy, 14° Bé. Other districts have been prospected but they yield little or nothing.

In Kern County we come to the largest field that has yet been discovered. It has developed marvelously, over 600 wells have been dug and nearly all are producers. Some of them yield only a few barrels a day but most of them are about 50-barrel wells.

Some have produced much more: 200, 400 or even 600 barrels a day. None of them are flowing. The average depth of the wells is about 800 feet; some are less than 500 feet, and the deepest are less than 1100 feet. The oil is thick, black and heavy, ranging in gravity from 9° Bé to 22° Bé., usually being from 14° to 17° Bé. It usually carries much fine sand, from which it is freed by settling. The oil is sometimes previously thinned by heating with steam. The oil carries large amounts of asphaltum, from 10 to 40 per cent. The present well-defined producing area of the Kern River district measures about 5 miles long and 3 miles wide, the longer axis extending in a northwesterly direction, and the thickness of the oil sand varies from 50 to 400 feet, a large proportion being of the latter depth. The limits of the field have probably not been reached, and in time the producing area will probably be enlarged. 20,000 to 25,000 barrels a day are shipped from this district, and this yield could be increased many fold, if there was a sufficient demand. Owing to the lack of demand and consequent low price of oil, many of the wells are not pumped, the owners waiting for better prices. A pipe line is being constructed by the Standard Oil Company from Bakersfield to their refineries at Point Richmond on San Francisco Bay, a distance of 280 miles. The pipe is 8 inches in diameter, covered with asbestos and buried. The reason for this is that the oil is so viscous at ordinary temperatures that it cannot be pumped. It must be heated, and at every pumping station, which are 27 miles apart, a heating plant is installed. The company has also built 100 37,500-barrel storage tanks at Bakersfield and two 75,000-barrel cement reservoirs. The large area of the field and the great thickness of the oil sand indicate that the life of the wells will be very long. The Kern River field is the most important in California and produces more than half the entire yield of the State.

Another part of Kern County where petroleum is found is the McKittrick district. Here are large deposits of asphaltum that are worked by the Southern Pacific Railroad. They have built a branch 65 miles long, terminating at Asphalto. This district contains a few good wells, but many are useless. Some give very large amounts of water. The oil is light, about 33°, and the yield is about 50,000 barrels a month. A third district in Kern County is the Sunset. This has also been worked for asphaltum for nearly ten years. It has lately been developed for oil. Over fifty

companies are operating; some have good wells, as much as 100 barrels a day, but most of them are barren. Nearly all are troubled with fine sand that caves in and chokes the wells and also remains in the oil. There is a great lack of water. What there is is usually salt or alkaline. Most of the oil is heavy, containing about 30 per cent. to 40 per cent. asphaltum of good quality. The asphaltum for a time was more valuable than the oil, owing to the lack of transportation. This has been remedied by the railroad building a branch line connecting at Bakersfield. The adjoining Midway district appears promising but as yet has not produced much.

The foregoing are the districts that produce practically all the oil in California. But it has been found in greater or less quantity in almost every county, and also in parts of Oregon, Washington, British Columbia and as far north as Alaska. Some of the counties in which prospecting has been carried on extensively are, all the southern counties and in San Benito, Monterey, Santa Clara, San Joaquin, San Mateo, San Francisco, Alameda, Contra Costa Napa, Sonoma, Colusa, Tehama, Mendocino, Humboldt and Shasta Counties. Occasionally the wells have been bored very deep. Some in Contra Costa and San Mateo are 1200 feet deep. There is a well in Humboldt in the Mattole district over 2000 feet deep. They have all yielded a small amount of oil, but there are no wells that give more than a few barrels a day. The oils along the coast from Santa Clara northwards in San Mateo, Mendocino and Humboldt Counties, and eastward to Colusa County, are very different in quality from the southern oils. They are lighter in color—usually yellow—lighter in gravity, varying between 19° Bé. and 40° Bé., and contain a paraffin residue, with little or no asphaltum.

To recapitulate, we find that oil is distributed over this entire western coast, but as yet practically the whole amount produced comes from a few districts in the southern part of California. The following table compiled by Mr. C. L. Yates for the State Mining Bureau, will illustrate this.

The statistics for last year have not been accurately compiled, but the total amount produced will be 13,000,000 barrels. In spite of this greatly increased supply, the price is gradually rising, and when the present long-term contracts have expired, the price will probably go still higher.

The method of boring wells is practically the same as used in

PETROLEUM PRODUCTION OF CALIFORNIA FROM 1897 TO 1901.

County.	1897. Product. Bbls.	1897. Value.	1898. Product. Bbls.	1898. Value.	1899. Product. Bbls.	1899. Value.	1900. Product. Bbls.	1900. Value.	1901. Product. Bbls.	1901. Value.
Fresno.....	70,140	$ 70,840	154,000	$ 154,000	439,372	$ 439,372	547,960	$ 547,960	525,433	$ 236,444
Kern	.....	.....	10,000	10,000	15,000	13,500	919,275	827,348	3,902,125	1,131,616
Los Angeles...	1,327,011	1,327,011	1,462,871	1,462,871	1,409,356	1,409,356	1,722,887	1,722,887	2,304,432	1,062,038
Orange	12,000	12,000	60,000	60,000	108,077	108,077	254,397	254,397	302,652	181,591
Santa Barbara .	130,136	130,136	132,217	112,549	208,370	191,288	183,486	165,138	203,616	113,385
Ventura.....	368,282	368,282	427,000	571,000	496,200	496,200	443,000	398,700	472,057	236,028
Miscellaneous .	4,000	10,000	3,000	6,000	1,500	3,000	248,945	236,498	.....	.....
	1,911,569	$1,918,269	2,249,088	$2,366,420	2,677,875	$2,660,793	4,329,950	$4,152,928	7,710,315	$2,961,101

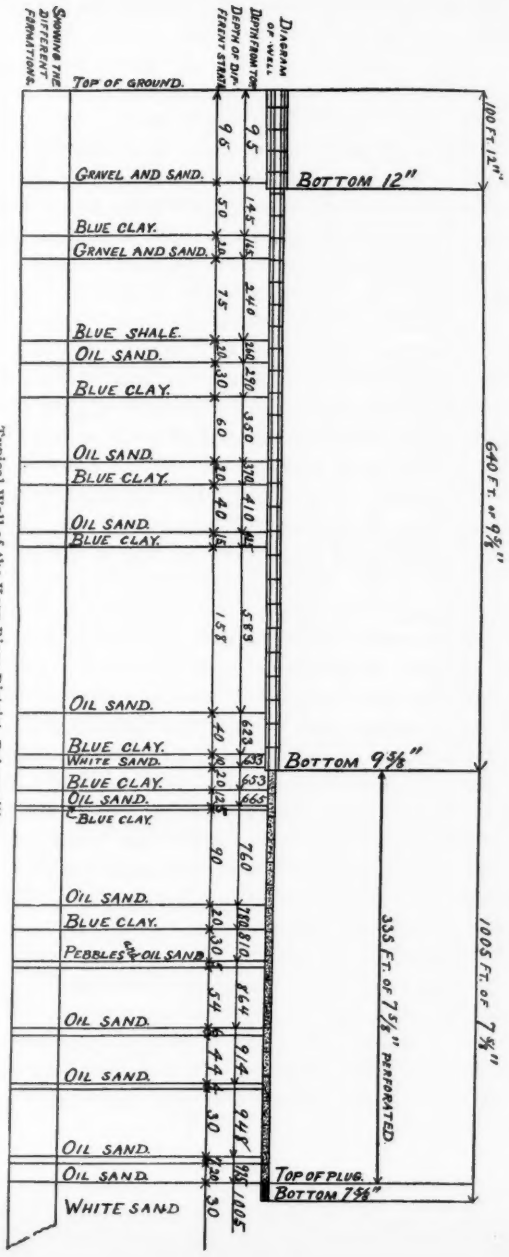
the east. The character of the formations passed through varies greatly according to the district. As the Kern River district is the largest, the following diagram showing a typical well is given.

There is apparently much difference in the quality of California petroleums obtained from different localities, but actually they are very much the same. The differences probably result from natural distillations or filtrations, a lighter oil being obtained, leaving a heavy residue containing asphaltum. Extreme variation is from 10° Bé. for oils of the McKittrick and Sunset district; to 35° Bé. for Coalinga and Puento. A water-white oil is found in the Newhall district that has a gravity of only 50° Bé. and leaves scarcely any residuum. It is evidently a natural filtrate or distillate. San Mateo, Colusa and Humboldt oils are apparently very different from most of the others, as they apparently contain little or no asphaltum. They have a gravity of from 17° to 50° Bé.

Chemically considered, California petroleums seem to be intermediate between Eastern and Russian oils. They contain paraffins, benzenes and naphthenes. Most of them contain nitrogen and sulphur. The sulphur seems to be contained in a volatile body, and is frequently almost entirely removed in a fraction boiling between comparatively narrow limits.

The chief use of California crude petroleum is for fuel. Many of the large steam plants have discarded coal and now burn oil. The annual consumption of coal in California has been nearly 2,000,000 tons, and nearly half of this has been displaced by oil. Crude oil in bulk does not burn readily, especially if it is heavy. A special form of burner must be used. The usual method is to inject the oil in a very fine spray, by means of steam, and the heated, finely divided particles will burn easily and completely.

As the flame is exceedingly hot, it is directed on to brickwork on the bottom of the fire-box, and the boiler heated to a large extent by radiation. The intense heat is wearing on the boilers, but the advantages of oil over coal, especially on this coast, are many. It is more convenient to handle,—it is cleaner and it is cheaper. The liquid oil is transported much more easily than the solid coal. When properly burned, there is no smoke or soot or cinders. There are no ashes, so the boiler tubes do not get stopped up. Oil-heating is particularly desirable for locomotive engines. Ease of loading and firing and absence of cinders, with consequent comfort to passengers, and no danger of setting fire to grain fields or



Typical Well of the Kern River District, Bakersville.

fences, are self-evident advantages. In Russia, nearly all the locomotives are thus run. Many of the engines in this state are oil burners, and it is only a question of time when practically all will be altered. The cheapness depends partly on the relatively greater economy in handling and partly on the greater heating value as compared with coal. Seven barrels of oil will weigh about a ton; at a cost of $1.25 per barrel, this would be equivalent to $8.90 per ton; at $1.50 per barrel, $10.50 a ton. But the heating value of oil, weight for weight, is greater than that of coal. From a number of experiments we have made in our laboratory, we find that the heating value of California oil is between 10,000 and 11,000 calories, averaging about 10,500. The best coals of this coast average 7,000 to 8,000 calories, and the usual steam coals much less. Comparing the cost of coal and oil at the above prices as to the theoretical heat value, a ton of oil would be worth $6.00 to $8.00 and the coal $8.00 to $9.00. The actual difference is very much greater than this, as there is much less waste in oil heating. From many actual experiments made under boilers, it has been found that from 4 to 4½ barrels of oil is equivalent to one long ton of good coal, a saving of from 25 per cent. to 40 per cent., so that coal cannot compete with petroleum at the present prices nor can it until its cost is reduced to between $4.00 and $5.00 a ton, whereas it is between $7.00 and $8.00 a ton, and the best qualities bring from $10.00 to $14.00. Oil is selling in San Francisco now at less than 70 cents a barrel. This brings the cost of fuel on this coast to a par with the cost in the east, with its consequent great advantages. The smelters around the bay are using oil with a saving of over 50 per cent. in the cost of fuel.

Outside of fuel, crude petroleum is used to a slight extent on this coast in gas-making, as a coarse lubricant and as an insecticide in the orchards. A comparatively small amount is thus consumed. The Elmore process for concentrating ores, which employs petroleum, may consume a quantity.

The refining of oil is conducted on an increasing scale. Thirty-three refineries are now in operation. The capacity varies from 50 to 2000 barrels a day, the aggregate amounting to from 8000 to 10,000 barrels daily. The usual distillates are made—benzines, illuminating and lubricating oils. None of these except the benzines are of very good quality. They are used chiefly to mix with eastern oils.

PHYSICAL CHARACTERISTICS OF CALIFORNIA PETROLEUMS.

Serial No.	District.	Color.	Gravities temperature. °C.	Corresponding °Bé.	Flashing-point. °C.	Burning-point. °C.
54	Los Angeles.	Black.	0.9589 at 15.0	16.1	115.5	134.0
116	Whittier.	"	0.9397	19.3	....	....
87	Ventura.	"	0.9460 " 22.0	18.3	73.0	80.2
155	"	"	0.9830 " 11.0	11.6	....	....
50	"	Brown.	0.9143 " 18.0	23.6	....	....
186	"	.....	0.9159 " 15.0	22.8	29.0	35.0
93	Newhall.	Water-white.	0.8059 " 19.0	45.0	....	....
156	Kern.	Black.	0.9572 " 18.5	15.7	....	....
157	"	"	0.9533 " 20.3	15.9	....	....
111	"	"	0.9760 " 18.0	13.5	....	....
112	"	"	0.9651 " 18.1	15.1	....	....
134	McKittrick.	"	0.9458 " 18.0	18.5	....	....
135	"	"	0.9628 " 18.0	15.4	....	....
103	Sunset.	"	0.9589 " 17.0	16.2	....	....
85	"	"	0.9245 " 18.0	22.0	....	....
149	Summerland.	"	0.9815 " 21.0	12.7	....	....
147	"	"	0.9792 " 21.0	13.0	....	....
160	Coalinga.	Brown.	0.9276 " 21.1	21.4	70.0	94.0
52	"	"	0.8962 " 26.2	27.0	....	....
51	"	"	0.9493 " 17.4	17.9	....	....
159	Santa Clara.	Light brown.	0.8515 " 18.0	34.4	89.5	104.0
184	San Mateo.	Brown.	0.9206 " 15.0	22.6	90.0	102.0
127	Santa Cruz.	Black.	0.9565 " 18.0	16.8	....	....
100	Napa.	Brown.	0.9603 " 18.0	16.0	131.0	138.0
98	"	Dark brown.	0.9655 " 18.0	15.1	135.0	140.0
154	Colusa.	Yellow.	0.8229 " 19.0	40.0	....	....
142	Contra Costa.	Black.	0.9653 " 17.0	15.1	....	....
161	Humboldt.	Red-brown.	0.8810 " 15.5	28.9	....	....
94	"	Yellow.	0.8992 " 18.0	26.3	41.0	44.0
95	"	"	0.8951 " 18.0	27.0	109.0	114.0
96	"	"	0.9489 " 19.0	17.9	101.0	117.0
99	"	"	0.7825 " 19.0	50.5	17.0	18.0
101	"	"	0.8263 " 15.0	40.6	less than 10.0	less than 10.0
187	.....	.....	0.9670 " 15.5	15.0	91.0	105.0

The asphalt residue is of excellent quality and finds a ready sale. In fact, in some cases, the oil was used for the asphaltum only, the distillates being rejected.

The future of the oil industry appears to be bright. The southern part of the state appears to contain a large supply of petroleum, particularly in the upper part of the San Joaquin valley. There is a large demand for fuel purposes alone, and there is little doubt but that uses for the distillates will be found. Benzene derivatives appear to be present in considerable quantities and it will pay to separate them. The greatest significance, however, will be the solution of the fuel problem.

As very little has been published in regard to the character of California oils, the following results may be of value. They have been compiled from analyses made in this laboratory during the past two years. They cover oils from the various districts, and serve to show the great variance in physical characteristics.

SPECIFIC VISCOSITIES OF CRUDE OILS AT 60° F. AND 185° F. = 15½° C. AND 85° C.

Sample number.	15.5° C. 60° F.	85° C. 185° F.	Sample number.	60° F.	185° F.
145	4.88	1.28	135	282.03	3.57
134	63.15	2.12	149	1462.83	8.35
157	299.59	4.70	160	11.19	1.54
161	1.57	1.05	95	3.00	1.15
101	1759.13	7.51	99	1.17	0.96
156	373.11	3.67	100	10.35	1.34
184	10.96	1.50	186	34.28	1.84
101	1.10	0.95	192	3259.27	9.00
112	274.35	3.35	187	347.77	3.37
2	19.40	1.60	4	16.96	1.53
138	396.72	4.28	113	142.66	2.85
189	310.56	3.38			

It will be noticed that the viscosity diminishes very rapidly as the temperature increases. At a temperature of 100° the viscosity approaches that of water or may even be less.

The following table shows the percentage of volatile matter at various temperatures. It is of value chiefly as showing the variant character of the oils from different districts. The analyses were carried out under practically the same conditions, and the results are comparative.

FRACTIONAL DISTILLATION OF CALIFORNIA PETROLEUM.

Serial number.[1]	District.	Water.	Below 100° C. " 212° F.	100° C. to 150° C. 212° F. to 302° F.	150° C. to 250° C. 302° F. to 482° F.	250° C. to 350° C. 482° F. to 662° F.	350° C. to asphalt. 662° F. to asphalt.	Asphalt.	Loss.
111	Kern.	1.4	0.00	0.00	3.9	34.0	27.2	31.6	1.9
112	Kern.	0.5	0.00	1.00	9.25	19.74	48.13	21.25	..
160	Coalinga.	0.00	0.00	1.10	21.70	40.70	21.50	14.60	0.4
99	Coalinga.	0.00	0.00	32.60	28.20	17.20	16.00	5.00	1.0
51	Coalinga.	1.00	0.00	0.80	15.00	42.50	14.50	25.40	0.8
52	Coalinga.	0.20	7.70	10.30	18.70	30.00	18.00	16.20	0.9
134	McKittrick.	0.00	0.00	0.00	19.10	20.80	45.82	14.25	..
135	McKittrick.	0.00	0.00	trace	8.50	23.50	53.25	15.00	..
85	Sunset.	0.00	0.00	6.50	17.26	17.25	47.98	11.00	..
103	Sunset.	0.00	0.00	0.00	11.90	26.40	37.80	23.90	..
87	Ventura.	2.74	....	....	....	....	....	....	..
155	Ventura.	9.50	0.00	0.00	11.20	34.05	8.75	36.50	..
50	Ventura.	0.00	0.00	17.00	11.50	9.00	21.50	41.00	..
186	Ventura.	0.00	2.50	9.50	16.00	54.50	2.20	13.80	1.5
101	Humboldt.	0.00	0.00	39.50	29.80	24.00	1.50	4.70	0.5
161	Humboldt.	0.00	0.00	0.00	47.50	35.20	9.60	7.50	0.2
94	Humboldt.	0.00	0.00	13.70	33.40	22.20	10.80	19.40	0.5
95	Humboldt.	0.00	0.00	0.00	15.70	35.10	44.30	4.90	..
96	Humboldt.	0.00	0.00	0.00	16.10	53.60	3.20	26.50	0.5
99	Humboldt.	0.00	5.20	27.40	28.20	17.20	16.00	5.00	1.0
100	Napa.	0.00	0.00	0.00	0.00	87.00	4.20	9.00	..
98	Napa.	0.00	0.00	0.00	0.00	15.70	72.60	11.40	0.3
154	Colusa.	0.00	0.00	0.00	8.80	96.00	21.60	0.50	0.1
93	Newhall	0.00	12.50	46.20	32.27	....	3.23	5.30	0.5
159	Santa Clara.	0.00	....	15.00	35.80	31.20	14.40	3.60	..
142	Contra Costa.	5.70	0.00	3.70	17.50	37.00	15.20	21.00	0.1
127	Santa Cruz.	21.50	0.00	0.00	6.20	34.00	14.40	22.80	1.1
149	Summerland.	25.00	0.00	0.00	6.50	17.10	27.50	22.50	1.4
184	San Mateo.	14.90	0.00	0.00	0.00	0.00	58.90	26.00	0.2

The percentage of carbon and hydrogen is shown in the following table: The difference is not put down as oxygen for the reason that most of the oils contain at times considerable quantities of nitrogen and sulphur.

Oil. Serial No.	Hydrogen. Per cent.	Carbon. Per cent.	Specific gravity.	District.
145	10.84	88.26	0.9700	Colusa.
114	11.30	85.80	.....	Bakersfield.
115	11.50	86.09	0.9397	Whittier.
155	10.81	80.42	0.9830	Ojai Valley.
170	12.16	84.86	0.9572	Kern.

[1] Numbers are volume per cent.

Oil. Serial No.	Hydrogen. Per cent.	Carbon. Per cent.	Specific gravity.	District.
156	10.72	86.32	0.9572	Bakersfield.
110	11.18	82.45	0.9760	Kern.
134	11.45	86.06	0.9458	McKittrick.
157	11.30	85.75	0.9533	Kern.
103	11.30	85.83	0.9589	Sunset.
142	10.83	84.66	0.9653	Contra Costa.
177	10.70	84.74	.....	.....
169	11.80	87.62	0.8620	Coalinga.
162	12.10	87.41	.....	.....
...	12.74	86.99	0.8059	.....
...	11.82	86.61	.....	.....
100	11.13	88.08	0.9603	Napa County.
161	12.03	86.69	0.8810	Humboldt.
159	12.88	86.08	0.8515	Santa Clara.

The percentage of sulphur and nitrogen is shown in the following table: Various methods were tried for the determination of the sulphur, but the most accurate and convenient was to effect the combustion of the oil in oxygen at twenty-five atmospheres pressure in a Mahler bomb, and determine the sulphuric acid produced. Apparently none of the sulphur escaped oxidation. On allowing the gases to pass through bromine water, the solution gave no trace of sulphuric acid.

The Kjeldahl method was used for determining the nitrogen. Oxidation was slow but complete.

SULPHUR AND NITROGEN IN CALIFORNIA PETROLEUMS.

Number.	Specific gravity.	Nitrogen. Per cent.
1	0.8254	0.001
103	0.9589	0.047
115	0.9306	0.669
169	0.8679	0.100
171	0.9774	0.0278
172	0.9629	0.185
174	0.8749	0.243
175	0.8801	0.204
150	0.9720	0.155
		Sulphur. Per cent.
154	0.8229	0.50
156	0.9572	0.80
157	0.9533	0.668
159	0.8515	0.920
169	0.8679	0.062
135	0.9628	0.880
134	0.9458	0.870
115	0.9397	0.700
112	0.9651	0.950
103	0.9589	0.86

The following table shows the calorific value of various California oils. The determinations were made in a Mahler bomb, with oxygen at 25 atmospheres pressure, in the usual manner.

CALORIFIC VALUE OF CALIFORNIA PETROLEUMS.

Number.	Specific gravity.	°Bé.	Calorific value. T. U. (calories.)	B. T. U.
103	0.9589	16.3	10.380	18,684
111	0.9760	13.5	10,190	18,342
112	0.9651	15.2	10,471	18,847.8
113	0.9518	17.5	10,350	18,630
115	0.9397	19.5	10,827	19,488.6
129	0.8861	28.6	10,800	19,440
134	0.9458	18.5	10,375	18,675
135	0.9628	15.6	10,317	18,570.6
...	0.9276	21.1	10,531	18,956
159	0.8515	34.4	11,192	20,145.6
145	0.9700	14.5	10,360	18,648
115	0.9397	19.3	10,725	19,305
156	0.9572	16.5	10,359	18,646.2
110	0.9760	13.5	10,263	18,473.4
157	0.9533	17.2	10,443	18,797.4
103	0.9589	18.0	10,380	18,684

Many more results of determinations might be given, but the foregoing serve to give an idea of some of the characteristics of California crude petroleum, and indicate the great diversity in physical properties. Chemically, they resemble each other much more closely, as will be shown in a subsequent paper.

CHEMICAL LABORATORY, UNIVERSITY OF CALIFORNIA,
BERKELEY, CALIFORNIA, January 9, 1903.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 83].

THE INFLUENCE OF ATMOSPHERIC OXIDATION UPON THE COMPOSITION AND ANALYTICAL CONSTANTS OF FATTY OILS.

BY H. C. SHERMAN AND M. J. FALK.

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IT is well known that the so-called non-drying and semi-drying as well as the drying oils may absorb oxygen from the air at ordinary temperatures and that the analytical constants are more or less changed by such oxidation. This subject was studied by Ballantyne[1] who found that olive, rape, cottonseed, arachis and linseed oils after exposure to sunlight in uncorked bottles showed

[1] *J. Soc. Chem. Ind.*, 10, 29 (1891).

lower iodine figures, higher specific gravities and higher temperature reactions with sulphuric acid. These changes took place without alteration of the volume of the oil and independently of the appearance of rancidity or free acid. In fact, there was no increase in acidity in olive, rape and arachis and only a very slight increase in the cottonseed and linseed oils.

Having found that such oxidation is less dependent upon sunlight and occurs more often in stored samples than is commonly supposed, we undertook a comparison of the changes produced in some of the constants to ascertain whether any quantitative relations could be traced which would enable one to judge the original nature of the oil from the results obtained upon a sample thus altered by exposure.

Samples of oils of about 200 grams each were allowed to stand for several months, with occasional shaking, in uncorked bottles, loosely covered to exclude dust, on a shelf in the laboratory which was frequently exposed to direct sunlight. No special effort was made to give the different samples the same amount of exposure and shaking since it seems impossible to control all the conditions which affect the rate of oxidation. These "exposed" samples were then compared with duplicate samples from the same packages which had been kept in well-filled, air-tight bottles or cans in a dark closet. Many of the oils had been analyzed when first received and in all such cases the agreement between the results first obtained and those found on the carefully protected samples was sufficiently close to show that no appreciable change had taken place in the latter.

The table which follows shows the changes which had taken place in the samples exposed to the air.

In each case there is a decrease in the Hübl figure (percentage of iodine absorbed) and an increase in specific gravity and temperature reaction with sulphuric acid. There is also, in each case, a slight increase in acidity and in the proportion of volatile acids present, but these changes are irregular and much too small to account for the changes in the other figures. These results show that the rise in temperature with sulphuric acid is not necessarily parallel with the Hübl figure and should not be used instead of the latter, but rather in connection with it. For instance, a sample of pure olive oil which had taken up oxygen from the air would, if judged by the high specific gravity and high temperature reaction,

be condemned as adulterated, whereas these results considered in connection with the low Hübl figure would at once indicate the true nature of the sample.

CHANGES PRODUCED IN ANALYTICAL "CONSTANTS" BY EXPOSURE TO LIGHT AND AIR.

Description of oil.	Specific gravity 15.5/15.5	Hübl figure.[1]	Temp. reaction. Maumené.[2]	Temp. reaction. Mitchell.[3]	Free acid as oleic.	Reichert-Meissl figure.
Olive oil (2058) fresh	0.917	83.8	100	16.9	2.65	0.43
" " " after exposure	0.923	77.4	127	20.3	3.27	0.75
Lard oil (2057) fresh	0.917	73.3	106	16.7	0.90	0.56
" " " after exposure	0.927	66.7	116	18.4	1.92	1.59
Cottonseed oil (2053) fresh	0.920	102.8	161	21.4	0.14	0.16
" " " after exposure	0.934	92.0	215	27.0	1.27	1.96
Cottonseed oil (2055) fresh	0.923	105.2	171	20.3	0.07	...
" " " after exposure	0.937	92.9	217	27.2	1.29	...
Maize oil (2056) fresh	0.924	117.2	174	...	2.78	0.60
" " " after exposure	0.935	107.0	216	...	4.59	1.40
Poppyseed oil (2069) fresh	0.923	125.3	202	25.2	2.75	...
" " " after exposure	0.931	117.1	214	27.7	3.63	...
Seal oil (2103) fresh	0.926	145.3	...	...	0.69	1.00
" " " after exposure	0.947	120.3	...	...	3.39	2.40
Linseed oil (2070) fresh	0.938	177.1	...	30.5	1.26	...
" " " after exposure	0.954	148.1	...	34.3	2.05	...
Linseed oil (2052) fresh	0.934	178.0	...	31.3	1.33	0.49
" " " exposed 4 months	0.942	165.8	...	...	2.23	1.10
" " " " 8 "	0.966	139.4	...	32.8	4.45	2.64

In the case of the linseed oil (No. 2025), where the greatest amount of oxidation had taken place, it seemed desirable to determine the effect upon the elementary composition to find if possible whether oxygen or hydroxyl had been added. In addition to the unchanged oil and the portion which had been exposed in a bottle for eight months, another portion which had been exposed in a thin layer until semi-solid was analyzed. The results were as follows:

[1] Determinations of the Hübl figure were carried out as previously described (this Journal, **23**, 168), using only the purest obtainable reagents and allowing always an excess of iodine about equal to the amount absorbed.

[2] Specific temperature reaction (referred to that of water as 100) on mixing 10 cc. of concentrated sulphuric acid with 50 grams of the sample.

[3] The figures in this column show the actual rise of temperature (in degrees centigrade) on mixing 10 cc. of concentrated sulphuric acid with a solution of 10 grams of the sample in 50 cc. of carbon tetrachloride.

	Carbon.	Hydrogen.	Oxygen.	Ratio C : H.
Linseed oil, unchanged.....	75.46	10.92	13.62	1 : 0.145
" exposed eight months..	73.23	10.46	16.31	1 : 0.143
" " till semi-solid..	69.03	10.06	20.91	1 : 0.146

In this case, therefore, the net result of the exposure was an increase in oxygen without any appreciable change in the ratio of carbon to hydrogen. This is practically in agreement with the experience of Bauer and Hazura in an experiment[1] in which a thin film of linseed oil was allowed to dry quite completely in the air.

It has already been shown[2] that atmospheric oxidation decreases the heat of combustion of fatty oils to an extent nearly proportional to, but slightly greater than, the increase in the specific gravity. This relation may now be explained somewhat more fully. The linseed oil (No. 2052) on exposure in bulk for eight months increased in specific gravity from 0.934 to 0.966 or 3.43 per cent., calculated on the original weight. The analyses show that it took up oxygen to the extent of 3.16 per cent. of its original weight. The greater increase in specific gravity is probably due to a slight contraction in volume. The original heat of combustion was 9364 calories per gram. Correcting for the increase in weight we have $9364 \div 1.0343 = 9053$ calories, but since the sample took up 3.16 per cent. of its weight of oxygen the "available hydrogen" must have been diminished by 0.395 per cent. of the original or 0.38 per cent. of the increased weight, requiring a further reduction of 131 calories. This gives an estimated heat of combustion for the exposed sample of 8922 calories per gram. Taking the increase in specific gravity as a direct measure of the oxygen absorbed, this calculated value would be 8910 calories. The value as determined by combustion in the bomb-calorimeter was 8899 calories per gram. These figures agree within the limits of experimental error and confirm the suggestion made in a previous paper that the heat of combustion taken in connection with the specific gravity may prove a useful factor in the study of the fatty oils.

With glycerides other than those having strong drying properties, it may be considered as practically established by the work of Hazura that the oxidation consists essentially in the addition of hydroxyl to the unsaturated fatty acids, oleic being converted into dioxystearic, and linolic into sativic acid. If, as stated by Ballan-

[1] *Monatsh. Chem.*, **9**, 459 (1888).
[2] This Journal, **23**, 164; **24**, 348.

tyne,[1] the oxidation takes place without change in volume, the increase in specific gravity due to the introduction of hydroxyl should be directly proportional to the decrease in iodine-absorbing power due to the saturation of the double bonds. The quantitative relation would then be:

Percentage increase in specific gravity: Decrease in Hübl figure :: OH : I, or as 17.008 : 126.85, or as 1 : 7.46.

Thus the sample of olive oil shown in the table above had increased in density from 0.917 to 0.923 or 0.65 per cent. The Hübl figure of the exposed sample was 77.4. Adding to this $7.46 \times 0.65 = 4.9$, we obtain as a corrected value 83.3 as against 83.8, the Hübl figure of the unchanged sample.

Correcting, according to the same proportion, the Hübl figures of all the "exposed" oils in the table we obtain the "recalculated" values given in Column III.

	Hübl figure.		
Sample.	I. In fresh condition.	II. After exposure.	III. Recalculated.
Olive oil (2058)	83.8	77.4	83.3
Lard oil (2057)	73.3	66.7	74.8
Cottonseed oil (2053)	102.8	92.0	103.3
Cottonseed oil (2055)	105.2	92.9	104.2
Maize oil (2056)	117.2	107.0	115.9
Poppyseed oil (2069)	125.3	117.1	123.6
Seal oil (2103)	145.3	120.3	137.2
Linseed oil (2070)	177.1	148.1	161.0
Linseed oil (2052) after 4 months	178.0	165.8	172.2
" (2052) " 8 "	178.0	139.4	165.0

In the first five samples, representing non-drying and semi-drying oils, the difference between the original and the recalculated Hübl figure is in no case greater than 1.5, while the difference for the average of the five samples is only 0.2 per cent. Poppyseed oil which is usually classed as a drying oil, but which is also edible, shows a discrepancy of 1.7 per cent. It appears, then, that with such oils the results obtained on an exposed sample may be recalculated according to the proportion above given, if either the original specific gravity or the original Hübl figure is known.

When neither of these is known, assume as the original specific gravity the average figure for the variety of oil under examination, calculate the apparent increase in specific gravity (in percentage of the original) and then recalculate the Hübl figure as above. If

[1] *Loc. cit.*

the oil is unadulterated, the recalculated Hübl figure should be within the limits of variation of pure fresh samples.

This method cannot be relied upon for oils containing the more highly unsaturated acids (drying oils, fish oils, etc.), since in such oils there is, as shown by analysis, either a direct absorption of oxygen as such or a condensation with elimination of water from the hydroxyl groups first added, probably accompanied by a slight contraction in volume.

As regards the examination of edible oils, however, the results here given may be said (1) to emphasize the importance of determining both the Hübl figure and the specific gravity, whatever other determinations are made, and (2) to show how the mutual relations of these constants enable one to interpret the results obtained upon samples greatly altered by exposure to atmospheric oxidation.

NEW YORK CITY,
May 1, 1903.

COMPOSITION OF THE "BREAK" FROM LINSEED OIL.[1]

BY GUSTAVE W. THOMPSON.

Received May 15, 1903.

FRESHLY pressed linseed oil, or linseed oil that has not been properly settled or prepared for the manufacture of varnish, when heated to, say, 400° Fahrenheit, undergoes a change which the varnish man describes as "breaking". The phenomenon consists in the appearance in the oil of gelatinous masses slightly darker than the oil itself, settling with difficulty and extremely difficult to remove from the oil by filtration. The bulk of the break appears in some instances to be very considerable. The following experiments, however, will show that the percentage, by weight, present is very small.

Twenty-five hundred grams of linseed oil were heated to the breaking-point. The oil was allowed to cool and then filtered. The precipitate clogged the filter considerably, which necessitated its removal to a glass vessel, in which it was washed with petroleum ether, by decantation. Finally, a non-oleaginous residue was obtained, weighing 6.93 grams, equal to 0.277 per cent. of the original oil. On ignition, a portion of this residue was shown to

[1] Read before the New York Section of the American Chemical Society, May 8, 1903.

contain 47.79 per cent. ash—equal to 0.1177 per cent. of the original oil. The oil, which was filtered from the break, was shown to contain 0.0039 per cent. ash. The following is an analysis of the ash from the break:

CaO	20.96
MgO	18.54
P_2O_5	59.85
SO_3	trace
	99.35

The first thing to note is that the phosphoric anhydride is present in the ash from the break in excess of what would form an orthophosphate when combined with the bases present. It appears, in fact, that the oxygen present in the phosphoric anhydride is to the oxygen in the bases in the ratio of 5 to 2, corresponding closely with that required by a pyrophosphate. The composition of the organic matter in this sample of break was not determined.

Ash determinations were made on a number of samples of oil, the following being a few of the results:

	Ash. Per cent.
No. 1, Fresh double-filtered raw American linseed oil	0.1429
No. 2, " " " " " " "	0.1967
No. 3, Good, well-settled " " "	0.0609
No. 4, Best American linseed varnish oil	trace

The ash from sample No. 1 was analyzed, with the following results:

	Per cent. of the oil.
CaO	0.0235
MgO	0.0221
P_2O_5	0.0705
K_2O	0.0043
SO_3	0.0227
	0.1431

It should be noted that here, also, the phosphoric acid, is in excess of the bases, and is present largely in the pyro form.

Mulder speaks of the presence of calcium sulphate in linseed oil, but, so far as we know, no mention has been made of the presence of phosphates.

In order to locate the origin of the constituents of the linseed oil ash, analyses were made of the ash from American flaxseed, and flaxseed cake made therefrom, which analyses are given here:

	Flaxseed. Per cent.	Oil cake. Per cent.
Ash	3.112	4.899
Composition of ash.		
SiO_2	1.83	1.51
$Fe_2O_3 + Al_2O_3$	1.25	1.59
CaO	9.46	9.24
MgO	18.31	18.52
K_2O	26.18	26.14
Na_2O	1.71	3.59
SO_3	3.96	3.51
P_2O_5	35.44	36.28
	98.14	100.38

These analyses confirm, in the main, analyses already published. If we consider the ratio between the oxygen in the bases and the oxygen in the phosphoric anhydride in an orthophosphate to be as 3 is to 5 we find here that the bases are in excess. It is worthy of notice here that the phosphoric acid, lime and magnesia are dissolved, to some extent, by the oil, while the potash, which is the principal base, is taken up by the oil, only to a very slight extent.

In examining the mucilage from various plants, Schmidt and Kirchner, and Tollens[1] reported the presence of phosphates in the mucilage which they separated from the flaxseed; it seems probable that these phosphates in the seed are largely combined with the mucilage, and that the mucilage and the phosphates combined therewith are dissolved, to some extent, by the oil. This conclusion, however, requires confirmation. Examining a portion of thoroughly extracted break for mucilage, we obtained no reaction. The test made was to heat the break with dilute hydrochloric acid for a few seconds, filter and add alcohol. No precipitate was obtained. It may have been that the mucilage was decomposed at the temperature to which it was subjected. We have not been able, as yet, to pursue our inquiries further along this line.

As to the presence of albuminoids in linseed oil, our experiments have been as follows: The determination of nitrogen in a sample of linseed oil showed less than 0.01 per cent. The same sample of oil showed 0.04 per cent. of phosphorus. This would indicate that, relatively speaking, the phosphates present were considerably greater than the nitrogenous matter. An examination, for nitrogen, of a portion of extracted break indicated that some was present although the amount was less than 1 per cent. of the break. The phosphorus, on the other hand, amounted to 9.60 per

[1] *Ann. Chem.* (Liebig), **51**, 175 and 215.

cent. of the break. This, figured to P_2O_5, amounted to 57 per cent. of the ash in the break. It would seem unjustifiable to calculate the phosphorus present in the linseed oil to lecithin, on account of the large percentage of bases present. Inasmuch as albuminoids coagulate at a low temperature as compared with the breaking temperature of linseed oil, we feel that any assumption that albuminoids are present is unjustified. We do, however, feel justified in saying that the principal cause of the break in linseed oil is the phosphates of lime and magnesia present, although their presence in the oil may be due to a combination between them and some organic base or bases.

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

ON A CLASS OF PSEUDOTHIOUREAS DESCRIBED AS NORMAL UREAS.

BY HENRY L. WHEELER AND GEORGE S. JAMIESON.

Received April 22, 1903.

WHEN thioamides are treated with alkyl halides, compounds are formed having the alkyl group attached to sulphur. In the normal thioureas, for example, it is the sulphur and not the nitrogen that is the point of attack. When a radical is attached to sulphur then further alkylation may take place on the nitrogen.[1] At least this has been found to be true in all cases that have been thoroughly examined.

There are some thioureas, however, that have been represented as yielding nitrogen alkyl derivatives with halides. Wunderlich[2] found that sodium cyanamide unites with mustard oils in alcoholic solution, giving the sodium salts of alkylcyanthioureas RNHCSNHCN, and by treating these salts with alkyl halides the sodium was shown to be replaced by alkyls. The resulting dialkyl compounds were represented by the general formula RNH—CSNR'CN.

Later, Hecht[3] prepared a large number of these compounds. He represents them by the formula above, but he remarks that further work will be necessary to determine their structure and he states that this will be the subject of a later paper. Thirteen years

[1] Bertram: *Ber. d. chem. Ges.*, **25**, 48 (1892).
[2] *Ber. d chem. Ges.*, **19**, 448 (1886).
[3] *Ber. d. chem. Ges.*, **23**, 1658 (1890).

have now passed and these compounds have not been further examined. From what has just been said, it seemed doubtful that the entering alkyl group attaches itself to nitrogen. We therefore undertook the determination of the structure of these ureas, and we will now show that they are incorrectly represented in the literature—that they are pseudothioureas and not derivatives of normal thioureas. Their structure is to be represented by the general formula

$$RN{=}C(SR'){-}NH{-}CN,$$

in which R′ is the alkyl of the alkyl halide.

Sodium cyanamide was treated in alcoholic solution with phenyl mustard oil. The crystalline salt thus obtained was heated with methyl iodide according to the directions of Hecht. The pure product melted, as he states, at 186°. When this was suspended in strong alcoholic ammonia, a reaction slowly took place and methyl mercaptan made its presence known. In order to get a complete reaction, it was necessary to heat in a closed tube at 90°-95°. The crystalline product was then free from sulphur and, on analysis, gave results agreeing with those calculated for phenylcyanguanidine. The reaction took place as follows:

$$C_6H_5N{=}C(SCH_3){-}NHCN + NH_3 = C_6H_5N{=}C(NH_2){-}NHCN + HSCH_3.$$

In addition to the above phenylcyanthiolmethylpseudothiourea, we have prepared and examined phenylcyanthiolbenzylpseudothiourea, the phenylthiocarbaminbenzylcyamide of Hecht. This compound has the structure

$$C_6H_5N = C(SC_7H_7) - NHCN.$$

We find also that it is identical with Fromm's phenyl-ψ-benzylsulphoharnstoffcyanide, a fact which apparently escaped the notice of Professor Fromm.[1] He gives the melting-point at 190°. Hecht states that the substance melts at 182°. We have prepared the compound by both methods and both preparations melted at 182°-183°. When mixed, the melting-point was not altered. We have also prepared the corresponding methyl deriva-

[1] *Ber. d. chem. Ges.*, **28**, 1304 (1895).

tive by both methods and find that these products are identical.

The preparation of Hecht's compounds by Fromm's method offers further proof that the compounds are pseudothioureas. This method consists in treating phenyldithiobiuret with three molecular proportions of alkyl halide and four of alkali. The reaction is represented as follows:

$$C_6H_5N{=}C(SNa){-}NHCS{-}NH_2 + C_7H_7Cl = C_6H_5N{=}C(SC_7H_7){-}NHCSNH_2$$

$$C_6H_5N{=}C(SC_7H_7){-}NHCSNH_2 + 2NaOH =$$

$$C_6H_5N{=}C(SC_7H_7){-}NHCN + Na_2S + 2H_2O.$$

Fromm has shown that when the phenylcyanthiolbenzylpseudothiourea is boiled with hydrochloric acid it takes up the elements of water and separates aniline, forming thiolbenzylallophanic ester, $C_7H_7S.OC{-}NHCONH_2$. This shows that the alkyl group is attached to sulphur.

The pseudothioureas containing a —CN group are more stable and less reactive than other pseudothioureas. They have acid properties and form salts even with ammonia.

It was found that phenylcyanthiolbenzylpseudothiourea could be crystallized unaltered from boiling acetic anhydride. Benzoyl chloride failed to react with the compound in the Schotten-Baumann process, and little or no mercaptan was given off on heating on the steam-bath or at 150° with aniline or with phenylhydrazine. These compounds, therefore, depart widely in properties from other classes of pseudothioureas.

Phenylcyanguanidine, $C_6H_5N{=}C(-NH_2){-}NHCN$.—Phenylcyanthiolmethylpseudothiourea was heated with an excess of alcoholic ammonia at 90°-95° for five hours. Mercaptan escaped, on opening the tube, and from the alcoholic solution bunches of colorless needles were obtained. These were moderately soluble in warm alcohol and could be crystallized from water. The substance dissolved in warm alkali and was precipitated by mineral acids. It melted at 190°-191° without decomposition, and a nitrogen determination gave:

	Calculated for $C_8H_8N_4$.	Found.
Nitrogen	35.0	35.2

The *ammonium salt* of phenylcyanthiolmethylpseudothiourea was obtained when the pseudothiourea was heated at 100° for five hours with alcoholic ammonia saturated with hydrogen sulphide. On cooling, no pressure was found in the tube and, on concentrating the solution, colorless needles separated which, after two recrystallizations, melted at about 142°-143° to a pale yellow liquid. A nitrogen determination gave:

	Calculated for $C_6H_5N=C(-SCH_3)-NHCN.NH_3C_9H_{12}N_4S$.	Found.
Nitrogen.....	26.82	26.79

NEW HAVEN, CONN., April 17, 1903.

THE BASIC OXALATES OF BISMUTH.

BY F. B. ALLAN.

Received May 20, 1903.

IN recent papers the author has given the results of researches on the nitrates[1] and sulphates[2] of bismuth, making use of the phase rule to determine the number of phases present, and thus to know whether the solid to be analyzed was one phase or a mixture of two phases. In a monovariant system of three components, we may have a gaseous, a liquid, and two solid phases. In a divariant system, only three phases can exist and there can be only one solid in addition to the liquid and gaseous phases, and it is only in the latter case that we can call the solid a chemical compound. In the experiments referred to, both monovariant and divariant systems were obtained, but as three weeks were sometimes necessary to obtain equilibrium in a monovariant system, no attempt has been made to get other than divariant systems in this research.

Heintz[3] added oxalic acid to a solution of bismuth oxide in nitric acid, and boiled the precipitate repeatedly with water. He supposed that the neutral oxalate is first formed, and that it is decomposed by water; he gives the resulting substance the formula $Bi_2O_32C_2O_31\frac{1}{2}H_2O$. Schwartzenberg[4] boiled bismuth oxide with acid potassium oxalate, and the product dried at 100° agreed with the formula $Bi_2O_33C_2O_34H_2O$. Souchay and Lensson[5] prepared the neutral oxalate and gave the composition of the air-dried salt

[1] *Am. Chem J.*, **25**, 307.
[2] *Ibid.*, **27**, 284.
[3] Pogg. *Ann.*, **63**, 90.
[4] *Ann. Chem.* (Liebig), **64**, 127.
[5] *Ibid.*, **105**, 245.

TABLE A.

Temp. 50°. $\frac{Bi_2O_3}{C_2O_3}$ { in $Bi_2O_3 3C_2O_3 = 2.15$. in $Bi_2O_3 2C_2O_3 = 3.23$.

Components.	Time.	Composition of solution.	$\frac{Bi_2O_3}{C_2O_3}$ in solid.
1 gram neutral oxalate.	100 cc. water.	3 days	0.0225 N. oxalic acid.	3.33
2 grams " "	100 " "	3 "	0.0435 " "	3.27
3 " " "	100 " "	3 "	0.0647 " "	3.26
4 " " "	100 " "	3 "	0.0857 " "	3.25
2 " " "	100 cc. 0.042 N. oxalic acid.	7 "	0.085 " "	3.25
2 " " "	100 " 0.019 " "	3 "	0.069 " "	2.21
2 " " "	100 " 0.14 " "	3 "	0.138 " "	2.15
2 " " "	100 " 0.21 " "	3 "	0.205 " "	2.16
2 " " "	100 " 0.34 " "	3 "	0.34 " "	2.12
2 " " "	100 " 0.70 " "	3 "	0.68 " "	2.12

as $Bi_2O_3 3C_2O_3 7\frac{1}{2}H_2O$, while Muir[1] gave it the formula $Bi_2O_3 3C_2O_3 6H_2O$. I could not obtain this salt free from the basic oxalate although it was stirred for several days with a concentrated oxalic acid solution. Souchay and Lensson boiled the neutral oxalate repeatedly with water and obtained the basic salt $Bi_2O_3 2C_2O_3 H_2O$, and Muir repeating this preparation gave it the formula $Bi_2O_3 2C_2O_3$.

In the following experiments, the neutral oxalate, containing some basic oxalate, was stirred with water or oxalic acid solutions, the apparatus used being the same as that previously described. The composition of the solid contents was determined by the analysis of the liquid phase.

TABLE B.
Temp. 75°.

Components.	Time.	Composition of solution.	$\frac{Bi_2O_3}{C_2O_3}$ in solid
1 gram neutral oxalate 100 cc. water	3 days	0.024 N. oxalic acid	3.35
2 grams " " 100 " "	3 "	0.046 " "	3.27
3 " " " 100 " "	3 "	0.068 " "	3.28
4 " " " 100 " "	3 "	0.090 " "	3.26
5 " " " 100 " "	3 "	0.122 " "	3.21
6 " " " 100 " "	3 "	0.135 " "	3.25

At 50° the basic salt is in equilibrium with oxalic acid solutions up to 0.085 normal, and at 75° up to at least 0.135 normal. In the sixth experiment in Table A the reaction is delayed by the initial strength of the oxalic acid solution. The basic salt obtained in these experiments was air-dried and dissolved in hydrochloric acid. The bismuth was determined as the sulphide and the oxalic acid in the filtrate was titrated directly with permanganate, as the small quantity of hydrochloric acid present did not effect the result.

	Calculated for $Bi_2O_3 2C_2O_3 H_2O$.	Found.
Bi_2O_3	74.16	74.14
C_2O_3	22.97	23.00
H_2O	2.87	(2.86)

Miller and Kenrick[2] have shown that the number of possible phases is not changed if a new constituent be added to the liquid phase, provided that this new constituent does not pass into the solid phase. This condition is fulfilled, if dilute ammonia is stirred with $Bi_2O_3 2C_2O_3 H_2O$, and therefore a divariant system

[1] *J. Chem. Soc.* (London), 1878, p. 193.
[2] Trans. Roy. Soc., Canada, 1901.

TABLE C.

Temp. 75°.

Components.									Time.	$\frac{Bi_2O_3}{C_2O_3}$ in solid.
1 gram	$Bi_2O_3 2C_2O_3H_2O$,	100 cc.	18	per cent.	NH_4NO_3	and	0.0275	N. NH_3	1 day	3.55
1 "	"	100 "	18	"	"	"	0.0457	"	1 "	3.84
1 "	"	100 "	18	"	"	"	0.091	"	1 "	5.28
1 "	"	100 "	3.6	"	$(NH_4)_2C_2O_4$	"	0.0275	"	1 "	3.20
1 "	"	100 "	3.6	"	"	"	0.0457	"	1 "	3.20
1 "	"	100 "	3.6	"	"	"	0.091	"	1 "	3.20

TABLE D.

Temp. 75°. $\frac{Bi_2O_3}{C_2O_3}$ in $3Bi_2O_32C_2O_3 = 9.69$.

Components.			Time.	Composition of solution.	$\frac{Bi_2O_3}{C_2O_3}$ in solid.
1 gram	$Bi_2O_32C_2O_3H_2O$.	100 cc. 0.028 N $(NH_4)_2C_2O_4$ and 0.0462 N. NH_3.	2 days	0.0703 N. oxalate (neutral).	8.82
1 "	"	100 " 0.028 " " " 0.0578 "	2 "	0.0720 " "	9.70
1 "	"	100 " 0.028 " " " 0.0693 "	2 "	0.0720 " "	9.70
1 "	"	100 " 0.028 " " " 0.0809 "	2 "	0.0720 " "	9.70
1 "	"	100 " 0.028 " " " 0.0925 "	2 "	0.0724 " "	9.79
1 "	"	100 " 0.028 " " " 0.104 "	2 "	0.0731 " "	9.90
1 "	"	100 " 0.028 " " " 0.115 "	2 "	0.0720 " "	9.70
1 "	"	100 " 0.028 " " " 0.138 "	2 "	0.0743 " "	10.50

still contains but one solid phase. In the following experiments, ammonia of varying strength was used and another basic salt was obtained. Preliminary experiments showed that the new basic salt was acted upon by quite dilute ammonia, and in order to obtain this solid phase in equilibrium with a larger range of concentrations of ammonia, it was necessary to reduce the efficiency of the ammonia in the reaction. This can be done by adding to the solution any ammonium salt, thus decreasing the amount of ionization, and as ammonium oxalate is one of the products of the reaction, it is the best salt for this purpose. Table C contains a comparison of the rate of reaction in the presence of ammonium nitrate and of ammonium oxalate, and shows that although the ammonium oxalate was more dilute, the reaction was much quicker in the ammonium nitrate solution.

Nos. 2 to 7 in Table D are divariant systems with one solid phase. The solid contents of these bottles were filtered off, air-dried, and analyzed.

	Calculated for $3Bi_2O_3 2C_2O_3$.	Found.
Bi_2O_3	90.64	90.42
C_2O_3	9.36	9.47

This basic salt has not been previously described.

TABLE E.

Temp. 50°.

Components.			Time.	$\frac{Bi_2O_3}{C_2O_3}$ in solid.
1 gram	$Bi_2O_3 2C_2O_3$	100 cc. 0.093 N. NH_3	4 days	1.16
1 "	"	100 " 0.465 "	4 "	2 21
1 "	"	100 " 0.07 N. KOH	4 "	6.63
1 "	"	100 " 0.10 "	4 "	Bi_2O_3.

Table E shows the results obtained when the higher basic oxalate reacts with more concentrated ammonia, or with potassium hydroxide. There is no indication of another basic salt.

Neutral bismuth oxalate was stirred with solutions of potassium oxalate and of ammonium oxalate, but the reaction was found to be slow, and it was difficult to obtain equilibrium. The composition of the solids obtained indicated the existence of double salts having the formulas $Bi_2(C_2O_4)_3(NH_4)_2C_2O_4$ and $Bi_2(C_2O_4)_3K_2C_2O_4$, and Souchay and Lensson's experiments in which they found more complex double salts were repeated, and the products analyzed by Messrs. DeLury and Phillips. Their results are published in this Journal.

CHEMICAL LABORATORY, UNIVERSITY OF TORONTO, May, 1903.

A NEW DOUBLE OXALATE OF BISMUTH AND POTASSIUM.

By F. B. Allan and J. S. DeLury.

Received May 20, 1903.

By dissolving bismuth oxalate in concentrated, hot potassium oxalate and cooling the solution, Souchay and Lensson[1] obtained a substance to which they gave the formula

$$Bi_2(C_2O_4)_3 7K_2C_2O_4 24H_2O$$

and from the mother-liquor they got a further deposit having the composition

$$Bi_2(C_2O_4)_3 11K_2C_2O_4 24H_2O.$$

Svensson[2] has also described a double salt having the composition

$$Bi_2(C_2O_4)_3K_2C_2O_4 2H_2O.$$

When a small quantity of bismuth oxalate is stirred with a saturated potassium oxalate solution, the solid phase is found to be potassium oxalate containing only a trace of bismuth, the bismuth oxalate having displaced the potassium oxalate in the solution. If more dilute solutions of potassium oxalate be used, the solid phase approaches the composition $Bi_2(C_2O_4)_3K_2C_2O_4$, but the double salt was not obtained pure in this way.

Bismuth oxalate was boiled with a 20 per cent. solution of potassium oxalate; the hot solution was filtered and, on cooling, deposited small, white crystals. These crystals, dried under pressure, were dissolved in hydrochloric acid and the solution, after the removal of bismuth, was evaporated to dryness, ignited, and the potassium determined as potassium chloride; the bismuth was determined as the sulphide and the oxalic acid by titration with permanganate.

	Calculated for $Bi_2(C_2O_4)_3K_2C_2O_4.9\frac{1}{2}H_2O$.	Found.
Bismuth	40.94	40.91
C_2O_4	34.56	34.54
Potassium	7.69	7.69
Water	16.81	(16.86)

A 21 per cent. and a 23 per cent. solution of potassium oxalate gave the same double salt. Bismuth oxalate was then boiled with a solution of potassium oxalate saturated at room temperature, and the deposit at 50° contained 36.1 per cent. C_2O_4 while that ob-

[1] *Ann. Chem.* (Liebig), **105**, 245.

[2] *Ber. d. chem. Ges.*, **3**, 314.

tained by cooling the same solution from 50° to room temperature contained 51.9 per cent. C_2O_4. As the oxalates described by Souchay and Lensson would contain 41.9 per cent. and 49 per cent. C_2O_4 respectively, it seems probable that the precipitates from the more saturated solutions are mixtures of the double salt described above and potassium oxalate.

CHEMICAL LABORATORY UNIVERSITY OF TORONTO, May, 1903.

A NEW DOUBLE OXALATE OF BISMUTH AND AMMONIUM.

BY F. B. ALLAN AND T. A. PHILLIPS.

Received May 20, 1903.

SOUCHAY AND LENSSON[1] dissolved bismuth oxalate in concentrated, hot ammonium oxalate solution and obtained, on cooling, a double salt to which they gave the formula

$$Bi_2(C_2O_4)_39(NH_4)_2C_2O_424H_2O.$$

Their analyses do not agree very closely with that formula, and as some experiments made in this laboratory threw doubt on the existence of this complex double salt, their work has been repeated.

A 4 per cent. solution of ammonium oxalate was boiled with bismuth oxalate, using a reflux condenser, for about half an hour, and filtered hot. On cooling, this solution deposited small, white crystals which were dried, under pressure, between paper. The salt was easily soluble in hydrochloric acid. The bismuth was determined as the sulphide, the oxalic acid by titration with permanganate, and the ammonia distilled over by boiling with potash, absorbed in hydrochloric acid and determined in the usual way.

	Calculated for $Bi_2(C_2O_4)_3(NH_4)_2C_2O_48H_2O$.	Found.
Bismuth	43.93	44.30
C_2O_4	37.08	36.85
Ammonium	3.81	3.78
Water	15.18	(15.07)

Bismuth oxalate is only slightly soluble in ammonium oxalate, and large quantities of the solution must be used in preparing the double salt, so that imperfect filtering or the slight solubility of basic salt formed during the boiling would account for the high value found for bismuth and the corresponding low values for oxalic acid and ammonia.

[1] *Ann. Chem.* (Liebig), **105**, 245.

More of the double salt was prepared by using ammonium oxalate solution saturated at 25°. The precipitate deposited at 50° gave 3.85 per cent. of ammonia and was, therefore, the same compound as the first, but when this solution cooled to room temperature, it yielded two kinds of crystals which, under the microscope, were identified as the double salt and ammonium oxalate, and it would appear that the salt described by Souchay and Lensson was a similar mixture.

CHEMICAL LABORATORY, UNIVERSITY OF TORONTO, May, 1903.

DOUBLE HALIDES OF TELLURIUM WITH THE ALKALOIDS.

BY VICTOR LENHER AND WINIFRED TITUS.

Received April 27, 1903.

IT has been previously shown[1] that the chloride and bromide of tellurium unite with the salts of the amines to form a series of double salts in which the types of H_2TeCl_6 and H_2TeBr_6 are consistently followed. The hydrogen of these acids may be considered as having been directly replaced by the complex ammonium group, or the tellurium halide may be looked at as uniting with the molecules of the hydrochloride or hydrobromide of the amine.

Following the same line of work with the alkaloids, there appear types which differ considerably from the first or most simple type.

In some cases 1 molecule of the alkaloid unites with 1 molecule of H_2TeCl_6 or H_2TeBr_6 while in others 2 molecules of the alkaloids unite with 1 molecule of the tellurium halogen acids. As a rule, the salts appear to follow the type of compounds that H_2PtCl_6 forms with the alkaloids, for example, with quinine there appear the salts $C_{20}H_{24}N_2O_2H_2PtCl_6 + H_2O$ and $C_{20}H_{24}N_2O_2H_2TeCl_6$, while with morphine $(C_{17}H_{19}NO_3)_2H_2TeCl_6$ is analogous to $(C_{17}H_{19}NO_3)_2H_2PtCl_6 + 6H_2O$.

However, the chloroplatinate usually crystallizes with water of crystallization while these new compounds are anhydrous.

The method of procedure for the formation of these compounds consists in adding a strong solution of tellurium dioxide in hydrochloric or hydrobromic acid to a concentrated solution of the alkaloid in the corresponding acid.

[1] This Journal, **22**, 136.

In most cases a thick, curdy precipitate immediately forms. This precipitate is best purified by recrystallization from hot, dilute acid solution. Inasmuch as the alkaloid chloride or bromide frequently separates out in the cold, the recrystallization must be done hot. Obtained under these conditions, the salts crystallized very well. As in the case with the halogen salts of the amines with tellurium, the alkaloids form yellow chlorides with tellurium chloride and red bromides with the bromide.

All of the salts obtained are permanent at the ordinary temperature, but are easily decomposed by heat. Water decomposes them all with precipitation of tellurous acid, while dilute acids readily dissolve them.

Analysis.—In order to determine the composition of the salts, the amount of halogen and tellurium in each was determined and in one salt a combustion for carbon and hydrogen was made. The halogen was determined as the silver salt and the tellurium was determined as element.

CHLORIDES.

Quinine Chlorotellurate, $C_{20}H_{24}N_2O_2.2HCl.TeCl_4$.—When a strong solution of tellurium tetrachloride is added to a strong solution of quinine in hydrochloric acid, a light, curdy precipitate forms. This salt can be readily recrystallized from hot dilute hydrochloric acid. It contains no water of crystallization; at 150° it begins to decompose. Water decomposes the substance at the ordinary temperature.

Analysis.—Calculated: Cl, 31.91; Te, 19.12; C, 36.01; H, 3.93. Found: Cl, 31.86, 31.91; Te, 18.55, 18.79; C, 35.77, 35.53, 36.26; H, 3.91, 3.74, 3.72.

Cinchonine Chlorotellurate, $(C_{19}H_{22}N_2O.2HCl.TeCl_4)$.—This salt forms light yellow crystals.

Analysis.—Calculated: Cl, 33.44. Found: Cl, 33.69, 33.64.

Strychnine Chlorotellurate, $(C_{21}H_{22}N_2O_2HCl)_2TeCl_4$, appears on recrystallization as large, bright yellow needles.

Analysis.—Calculated: Cl, 21.05; Te, 12.61. Found: Cl, 21.32, 21.03, 21.20, 21.14; Te, 13.13.

Morphine Chlorotellurate, $(C_{17}H_{19}NO_3HCl)_2TeCl_4$.—This substance appears as dark yellow crystals, and is the most stable of the series toward heat.

Analysis.—Calculated: Cl, 23.30; Te, 13.97. Found: Cl, 23.13, 23.67; Te, 14.21.

Theobromine Chlorotellurate, $(C_7H_8N_4O_2HCl)_2TeCl_4$.—On bringing together the acid solution of the alkaloid and tellurium tetrachloride, no precipitate appears as with the other substances, but, on standing, the light yellow salt separates.

Analysis.—Calculated: Cl, 30.44; Te, 18.25. Found: Cl, 30.59, 30.55; Te, 18.59.

Brucine Chlorotellurate, $(C_{23}H_{26}N_2O_4HCl)_2TeCl_4$.—This salt appears as light yellow crystals.

Analysis.—Calculated: Cl, 18.81. Found: Cl, 18.36, 18.90.

With aconitine and atropine, non-crystalline bodies were first formed but quickly decomposed.

BROMIDES.

Quinine Bromotellurate, $(C_{20}H_{24}N_2O_2 2HBr)TeBr_4$.—This salt forms bright red crystals and is easily decomposed by heat.

Analysis.—Calculated: Br, 51.32; Te, 13.67. Found: Br, 51.27, 51.60; Te, 14.09.

Cocaine Bromotellurate, $(C_{17}H_{21}NO_4HBr)_2TeBr_4$.—The salt crystallizes readily in large carmine-red needles. It is quite readily decomposed by heat.

Analysis.—Calculated: Br, 39.47; Te, 10.48. Found: Br, 39.59, 39.14; Te, 11.18.

Brucine Bromotellurate, $(C_{23}H_{26}N_2O_4HBr)_2TeBr_4$.—This salt appears as brick-red crystals.

Analysis.—Calculated: Br, 34.26; Te, 9.12. Found: Br, 34.21, 33.80; Te, 8.50.

Morphine Bromotellurate, $(C_{17}H_{19}NO_3HBr)_2TeBr_4$.—This salt appears as dark red crystals.

Analysis.—Calculated: Br, 40.70; Te, 10.81. Found: Br, 40.42; Te, 10.70.

ON CERTAIN FACTORS INFLUENCING THE PRECIPITATION OF CALCIUM AND MAGNESIUM BY SODIUM CARBONATE.

BY J. M. STILLMAN AND ALVIN J. COX.

Received March 30, 1903.

THE data contained in the following communication were obtained in an investigation undertaken primarily to determine some of the conditions which modify the results of the usual processes

for the purification of water for boiler-feed purposes. In many of the waters of the more or less arid regions of this country the calcium and magnesium salts are present in large quantity, and experience has shown that the usual methods of purification by the use of lime and sodium carbonate give variable results. To determine, if possible, some of the conditions affecting the problem, the experiments here described were undertaken. The data obtained are but a contribution to the problem stated, but they have also application to other than the particular technical problem mentioned.

I. INFLUENCE OF SALTS OF SODIUM UPON THE PRECIPITATION OF CALCIUM AND MAGNESIUM BY SODIUM CARBONATE.

Solutions of calcium chloride and of magnesium chloride were prepared of such concentration that 25 cc. of the calcium solution gave 0.3285 gram calcium oxide, and 25 cc. of the magnesium solution yielded 0.6410 gram magnesium pyrophosphate.

In each test 25 cc. of one of these solutions were placed in a 100 cc. flask, the desired quantity of sodium chloride or sodium sulphate added in the form of a standardized solution, sodium carbonate then added in solution, so that unless otherwise specified 1.2 molecules of sodium carbonate should be present for each molecule of calcium chloride or magnesium chloride present. Larger excess was avoided as being foreign to the problem immediately under consideration. Water was added to make the volume to 100 cc. All conditions of manipulation were made as nearly equal as possible.

A. Influence of Sodium Chloride upon the Precipitation of Calcium.—Two series of tests were made with varying quantities of sodium chloride. In each series, 0, 2, 4, 6, 8 molecules of sodium chloride were added for each molecule of calcium chloride, and then the slight excess of sodium carbonate was added and the flasks filled to 100 cc. One series was then brought to the boiling-point and maintained there for three minutes; the other was not heated. Both series were then allowed to stand at room temperature for seven days.

At the end of this time the contents of the flasks were filtered and the filtrate tested for calcium with ammonium oxalate. No determinable amount of calcium was present, and it was therefore concluded that the presence of sodium chloride has no important

influence upon the precipitation of dilute calcium chloride solutions by sodium carbonate.

B. Influence of Sodium Chloride and Sodium Sulphate upon the Precipitation of Magnesium.—Twenty-five cc. of the above-mentioned magnesium solution were treated in a similar manner with 1.2 molecules sodium carbonate after addition of 0, 2, 4, 6, 8, or 10 molecules of sodium chloride. Duplicate series were prepared as before and one boiled for three minutes, the other not. At the end of seven days' standing the solutions were filtered, the magnesium determined as pyrophosphate in 50 cc. of the filtrate, and the entire amount remaining in solution estimated. The following results were obtained:

Mols. NaCl for 1 mol. $MgCl_2$.	$Mg_2P_2O_7$ in sol. per 100 cc. Boiled samples. Gram.	Not boiled. Gram.
0	0.3486	0.4350
2	0.4278	0.4766
4	0.4378	0.4988
6	0.4510	0.5150
8	0.4700	0.5356
10	0.4892	0.5590

Total amount magnesium as $Mg_2P_2O_7$ per 100 cc. before precipitation = 0.6410 gram. The influence of sodium chloride in diminishing the precipitation is here evident, and the brief heating increases the precipitation. It may be here stated that a preliminary experiment similar to the foregoing gave figures showing similar relations. In that test, however, the samples stood but four days, and equilibrium was not sufficiently attained.

With sodium sulphate the following data were obtained, the conditions of experiment being otherwise as with the preceding.

Mols. Na_2SO_4 for 1 mol. $MgCl_2$.	$Mg_2P_2O_7$ in sol. per 100 cc. Boiled. Gram.	Not boiled. Gram.
0	0.3486	0.4350
2	0.4846	0.5568
4	0.5816	0.6218
6	0.5874	0.6412 no precipitate.
8	0.5874	0.6406 " "
10	.....	..... " "

Total amount magnesium as $Mg_2P_2O_7$ per 100 cc. = 0.6410 gram.

The influence of the sodium sulphate is here again well marked, but seems to reach its maximum under the conditions of this experiment at about 6 molecules of sodium sulphate to 1 molecule mag-

nesium chloride, and here, as before, the short boiling influences the condition of equilibrium. The curves in Fig. 1 will illustrate

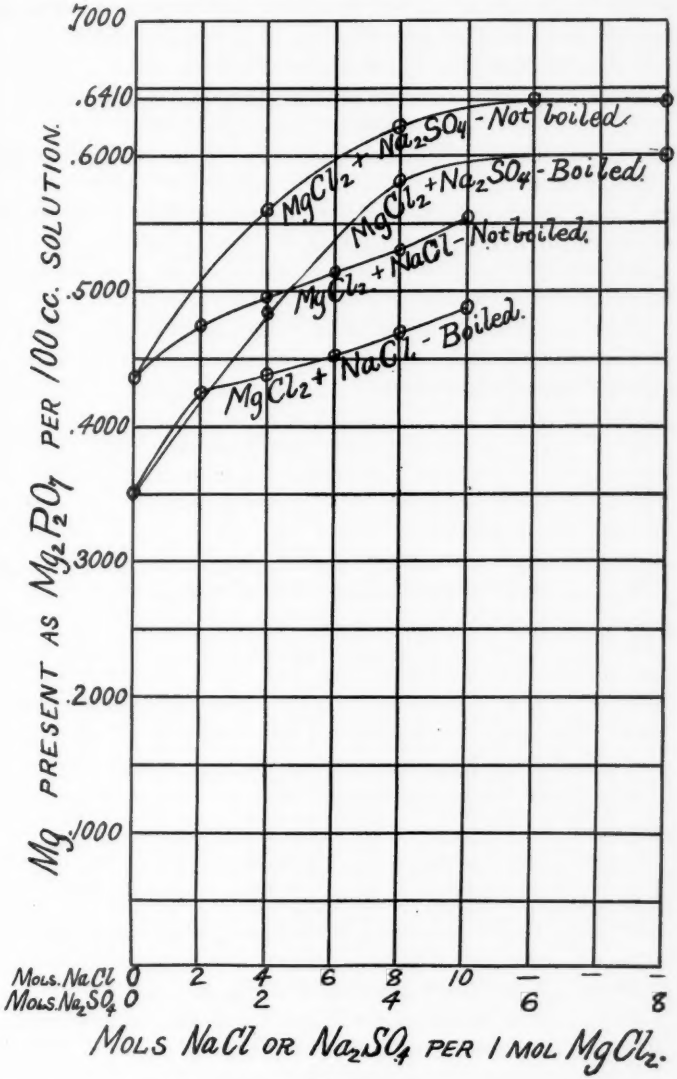
.7000
.6410
.6000
.5000
.4000
.3000
.2000
.1000
Mg. PRESENT AS $Mg_2P_2O_7$ PER 100 CC. SOLUTION.
$MgCl_2 + Na_2SO_4$ - Not boiled.
$MgCl_2 + Na_2SO_4$ - Boiled.
$MgCl_2 + NaCl$ - Not boiled.
$MgCl_2 + NaCl$ - Boiled.
Mols. NaCl 0 2 4 6 8 10 — — —
Mols. Na_2SO_4 0 2 4 6 8
MOLS NaCl OR Na_2SO_4 PER 1 MOL $MgCl_2$.

Fig. 1.

these relations. In order to bring out more clearly the relations, equivalent quantities of the two salts are coincident on the abscissas of the curves. It will be noticed that the sodium sulphate appears to exert a greater influence in preventing precipitation than the equivalent quantity of sodium chloride.

II. THE INFLUENCE OF TIME ON PRECIPITATION UNDER VARYING CONDITIONS.

This factor evidently has a direct bearing on the problem of water purification.

A magnesium solution was prepared containing magnesium equivalent to 0.6520 gram $Mg_2P_2O_7$ in 25 cc. The quantities of magnesium precipitated by sodium carbonate at different time intervals were determined under varying conditions.

First.—In solutions maintained at boiling temperature. For this purpose, the solutions were heated in pressure-bottles immersed in a boiling salt-water bath, the temperature of the bath being maintained at 102°-104° C. Three series were heated in this way.

(*a*) Twenty-five cc. of the magnesium solution (equivalent to 0.6520 gram magnesium pyrophosphate) were treated with 1.2 molecules sodium carbonate per 1 molecule magnesium chloride, and made up to 100 cc.

(*b*) Twenty-five cc. were treated as above, after addition of 4 molecules sodium sulphate to 1 molecule of magnesium chloride.

(*c*) Twenty-five cc. were treated as before, but with 10 molecules of sodium chloride instead of the sulphate. At intervals, the pressure bottles were removed from the bath, the contents thrown on a filter, and 50 cc. of the filtrate used for determination of magnesium. The data are calculated to a basis of 100 cc. of solution.

MAGNESIUM REMAINING IN SOLUTION AS $Mg_2P_2O_7$ PER 100 CC.

Hours.	Gram.	Hours.	Gram.	Hours.	Gram.
After 1/4	0.1176	1/4	0.2246	1/4	0.1634
" 1/2	0.1036	1/2	0.1946	1/2	0.1498
" 1	0.0740	1	0.0960	3/4	0.1322
" 2	0.0164	2	0.0832	1	0.0698
" 3	0.0108	3	0.0726	2	0.0522
"		4	0.0716	3	0.0420
"				4 1/4	0.0406

These data are shown graphically in Fig. 2.

Second.—The course of the reaction was studied in solutions maintained at room temperature without agitation.

For this purpose flasks containing 700 cc. of the various mix-

tures were immersed in a bath of running water, and the temperature thus kept within a narrow range of variation. At intervals, samples were removed by a pipette and filtered, and the magnesium remaining in solution was determined in 50 cc. of the filtrate.

The magnesium solution used was the same as last described, and the solution of calcium chloride used contained the equivalent of 0.3285 gram calcium oxide per 25 cc. The proportions employed in the different mixtures are given as per 100 cc. of the mixed solutions, though much larger quantities were made up.

The following series of tests were made:

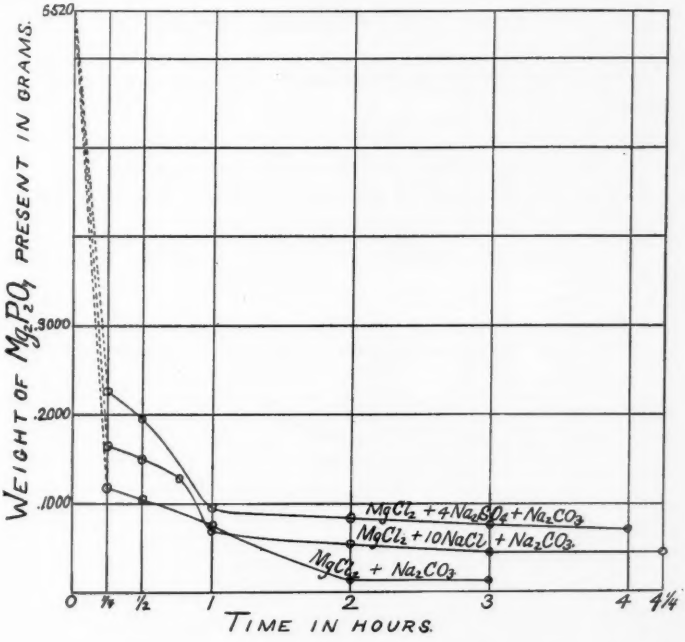

Fig. 2.

A.—Twenty-five cc. of the calcium solution were treated with 1.2 molecules of sodium carbonate and made up to 100 cc.

The calcium as calcium oxide remaining in solution after various time intervals was found as follows:

Of the total 0.3290 gram calcium oxide present, all but about 3 per cent. was precipitated in less than one-fourth hour.

Hours.	Calcium oxide. Gram.
After 1/4	0.0104
" 3/4	0.0104
" 1 1/4	0.0100
" 2	0.0083
" 3	0.0076
" 4 1/4	0 0062
" 6 1/4	0.0044
" 8 1/4	0.0032
" 20 1/4	0.0000

B.—The magnesium chloride was treated under the following varying conditions:

(*a*) Twenty-five cc. with 1.2 molecules of sodium carbonate to 100 cc. solution.

(*b*) The same mixture with addition of 10 molecules of sodium chloride.

(*c*) The same with 4 molecules of sodium sulphate.

(*d*) The same with 10 molecules of sodium sulphate.

Magnesium remaining in solution at varying time intervals as $Mg_2P_2O_7$ per 100 cc. was determined as follows:

Total quantity as $Mg_2P_2O_7$ per 100 cc. of solution was 0.6520 gram.

Hours.	(*a*). Gram.	(*b*). Gram.	(*c*). Gram.	(*d*).
After 1	0.4152	0.5270	0.5982	No precipitate.
" 3	0.4084	0.5252	0.5832	" "
" 6 1/2	0.4104	0.5216	0.5908	" "
" 12	0.3924	0.5072	0.5760	" "
" 22	0.3782	0.4880	0.5654	" "
" 32	0.3810	0.4882	0.5550	" "
" 46	0.3154	0.4484	0.5560	" "
" 60 1/2	0.2358	0.3966	0.5542	" "
" 80 1/2	0.1634	0.3094	0.5498	" "
" 107 1/2	0.1278	0.2320	0.4824	" "
" 131 1/2	0.1240	0.2204	0.3928	" "

These data are illustrated in the curves of Fig. 3. The variations in temperature are noted on the upper margin of the chart. It will be noticed that the temperature was not quite constant, and this fact may be partly responsible for the irregularities of the curves.

Third.—The influence of continuous agitation upon the course of the reaction.

For this purpose the bottles containing the mixtures were sub-

mitted at room temperature to violent agitation by means of a mechanical shaker operated by a motor. Three series were thus treated:

(*a*) A magnesium chloride solution containing the equivalent of 0.6871 gram magnesium pyrophosphate per 25 cc. was treated as before with sodium carbonate and diluted to 100 cc. for each 25 cc. of the magnesium solution.

(*b*) The same mixture after addition of 10 molecules of sodium chloride.

(*c*) The same mixture after addition of 4 molecules of sodium sulphate.

The shaking was interrupted at intervals for removing samples, and, as before, magnesium was determined in the filtered samples and the results calculated to a basis of 100 cc.

MAGNESIUM AS $Mg_2P_2O_7$ PER 100 CC. SOLUTION UNPRECIPITATED.

Hours.	(*a*). Gram.	(*b*). Gram.	(*c*). Gram.
After 3 1/4	0.4364	0.5288	0.6476
" 7 1/2	0.4216	.....	0.6384
" 13 1/4	0.1684	0.5084	0.6200
" 20 3/4	0.1464	0.4092	0.6224
" 34	0.1432	0.2360	0.4316
" 47	0.1364	0.2292	0.3380
" 61	0.1372	.....	0.3260
" 76	0.1368	0.2300	0.3200
" 99 3/4	0.1372	.....	0.3320

In the curves in Fig. 3 these data are plotted after recalculating to correspond to a total content before precipitation of 0.6520 gram instead of 0.6871 gram magnesium pyrophosphate per 100 cc., so that the curves may be better compared with the other data given on the chart. On the same diagram are also reproduced for comparison the data of Fig. 2. Comparison of these curves will show that in every case the influence of the presence of sodium chloride or sulphate is to diminish the precipitation of magnesium by sodium carbonate, and in these tests the sulphate exerts a greater influence in this direction than an equivalent quantity of the chloride. It would be premature, however, to draw any sweeping quantitative generalizations from these few comparisons. Even attempts to duplicate as exactly as possible the conditions of such a series as any one of the above, so far as our experience goes, do not give the same quantitative relations. The reason for this is easily seen in the difficulty of equalizing all conditions to which the

establishment of equilibrium is sensitive. On the other hand, the general relations of the influence of the above-mentioned salts and of temperature and agitation upon the precipitation of magnesium by sodium carbonate seem to be quite clearly established.

It is well-known that for the separation of magnesium in water-purification, calcium hydroxide is a much more effective precipitant than sodium carbonate. In order to obtain an approximate notion of the relation of this reaction to such data as above obtained, a single series of experiments was executed.

A magnesium choride solution was treated with a clear solution of calcium hydroxide (free from alkalies), with and without the presence of sodium chloride, and the same quantities of the same

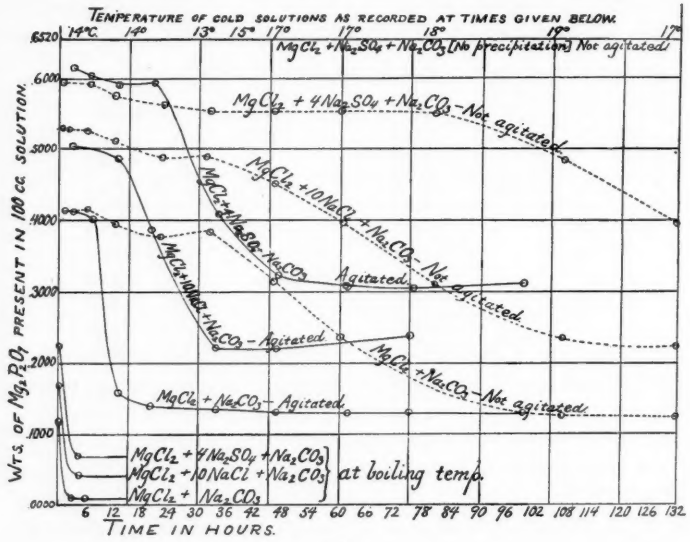
TEMPERATURE OF COLD SOLUTIONS AS RECORDED AT TIMES GIVEN BELOW.
14°C. 14° 13° 15° 17° 17° 18° 19° 17°
MgCl2 + Na2SO4 + Na2CO3 [No precipitation] Not agitated
MgCl2 + 4Na2SO4 + Na2CO3 - Not agitated.
MgCl2 + 10NaCl + Na2CO3 - Not agitated.
MgCl2 + Na2CO3 - Agitated.
MgCl2 + Na2CO3 - Not agitated.
MgCl2 + 4Na2SO4 + Na2CO3
MgCl2 + 10NaCl + Na2CO3
MgCl2 + Na2CO3
at boiling temp.
WTS. OF Mg2P2O7 PRESENT IN 100 CC. SOLUTION.
6320 6000 5000 4000 3000 2000 1000 0000
6 12 18 24 30 36 42 48 54 60 66 72 78 84 90 96 102 108 114 120 126 132
TIME IN HOURS.

Fig. 3.

solution were treated under the same conditions with an equivalent quantity of sodium carbonate. Owing to the greater insolubility of calcium hydroxide, it was necessary to use a more dilute magnesium solution.

The magnesium solution contained 0.2063 gram as $Mg_2P_2O_7$ in 3.750 cc.

The calcium hydroxide solution contained 0.00144 gram as CaO per cubic centimeter.

Mixtures were made as follows:

(a).	(b).	(c).	(d).
3.75 cc. $MgCl_2$	3.75 cc. $MgCl_2$	3.75 cc. $MgCl_2$	3.75 cc. $MgCl_2$
77.75 cc. CaO (1.1 mol.)	do.	4.07 cc. Na_2CO_3 (1.1 mol.)	do.
18.50 cc. H_2O	18.50 cc. NaCl (10 mol.)	92.18 cc. H_2O	18.50 cc. (10 mol.) NaCl
			73.68 cc. H_2O
100.00	100.00	100.00	100.00

The data are here given per 100 cc., although larger quantities (400 cc.) were actually used. These solutions were kept agitated by the mechanical shaker at room temperature and sampled at intervals. The following quantities of magnesium pyrophosphate per 100 cc. were found in the filtered samples.

Total amount of $Mg_2P_2O_7$ per 100 cc. is 0.2063 gram.

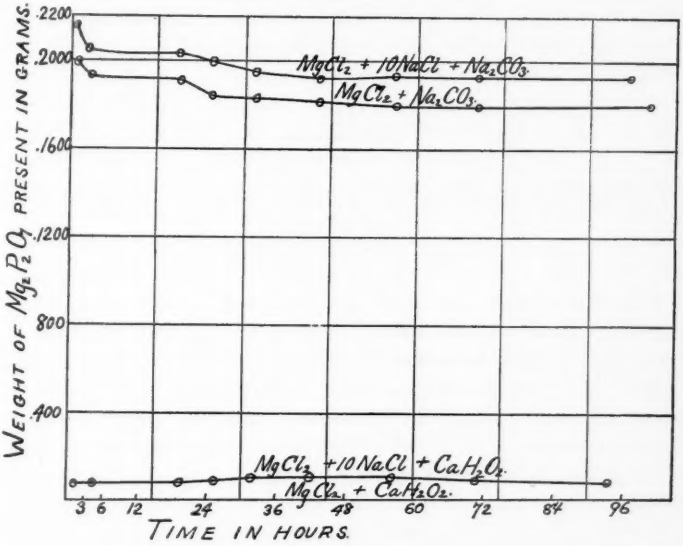

Fig. 4.

Hours.	(a). Gram.	(b). Gram.	(c). Gram.	(d). Gram.
After 1 1/4	.....	.....	0.1984	0.2124
" 1 1/2	.....	0.0080	.....	.....
" 1 3/4	0.0000	.....	.....	. . .
" 4 3/4	0.0000	0.0076	0.1936	0.2048
" 19 1/2	0.0000	0.0072	0.1908	0.2028
" 25 1/2	0.0000	0.0080	0.1844	0.1996
" 31 3/4	0.0000	0.0100	0.1828	0.1956
" 43 1/2	0.0000	0.0096	0.1820	0.1928
" 56 1/2	0.0000	0.0084	0.1788	0.1928
" 71	0.0000	0.0080	0.1780	0.1928
" 93 3/4	0.0000	0.0080	.....	0.1928
" 99 3/4	0.0000	.....	0.1792	.....

The foregoing data are produced graphically in Fig. 4. It will be noted that sodium chloride appears to have some influence on the precipitation of magnesium by calcium hydroxide, but that nevertheless the precipitation is quite complete. In the parallel tests with sodium carbonate, the amount of magnesium held in solution by sodium chloride is less in proportion to the entire amount present than was the case in the preceding experiments with solutions of somewhat greater concentration. In the more dilute solution, only about 6 per cent. of the magnesium present was held in solution, while in the less dilute about 15 per cent. was held in solution by 10 molecules of sodium chloride.

There is no intention to draw any generalizations from the single experiment with calcium hydroxide. Other experiments are in progress in this laboratory which may form the subject of a further communication on similar lines.

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THE DETERMINATION OF CARBONIC ACID IN DRINKING-WATER.

BY FRED B. FORBES AND GILBERT H. PRATT.

Received April 27, 1903.

IN the course of an investigation of the action of the various public water supplies of Massachusetts upon metallic pipes, it became desirable to know the amount of free carbonic acid contained in these waters at different times, as the results of many experiments indicated that this substance was in a large measure responsible for the action of water upon pipes, especially those of lead.[1]

Carbonic acid, as is well known, may exist in natural waters in three forms: Fixed carbonic acid combined directly with the alkaline earth bases, calcium oxide and magnesium oxide, to form normal carbonates, half-combined carbonic acid, and free carbonic acid.

The actual existence of bicarbonates of calcium and magnesium in solution has never been absolutely proven, as these salts have never been isolated; but for all practical purposes these compounds may be assumed to exist, as the behavior of the normal carbonates in solution in the presence of an excess of carbonic acid leads strongly to this conclusion.

[1] Report of Massachusetts State Board of Health, 1898, 541; 1900, 487.

If more carbonic acid than is necessary to form bicarbonates with the alkaline earth bases is present, it remains dissolved in the water in the free state, and is generally considered as a true acid with the formula H_2CO_3.

When a water containing free and half-bound carbonic acid is heated, the free acid is easily driven off. On boiling, the half-bound acid may also be expelled, though completely with some difficulty, resulting in the precipitation of the normal carbonate with which it was combined.

The method for the determination of carbonic acid originally used in the investigation was the well-known Pettenkofer method,[1] which determines the sum of the free and half-bound. For the separation of the free from the half-bound, a modification devised by Dr. T. M. Drown and which will be described later was employed. It was early seen that in the Pettenkofer method, when carried out as directed in most works on analytical chemistry, there were several sources of considerable error, and some modifications were introduced in order to avoid these errors.

During the course of our work the very excellent paper on "The Estimation of Carbonic Acid in Water" by J. W. Ellms and J. C. Benecker[2] appeared, recommending the Lunge-Trillich or Seyler method,[3] and experiments were made by us with this method, and also with the method of boiling off the carbonic acid directly, and absorbing in potash bulbs. This latter method is not practicable from a water analyst's point of view, as it requires an apparatus too complicated for use in the field, and all determinations of free carbonic acid to be of value must be made at the source of supply, as a water, after being drawn, very soon loses a considerable part of its dissolved carbonic acid. This method has been used, however, as a check on the other two, in experiments upon natural waters whose carbonic acid contents were unknown.

It is the purpose of the following pages to give an account of a series of results obtained with the three methods, and to point out some of the errors in each.

THE PETTENKOFER METHOD.

The usual mode of procedure is given by Sutton[4] as follows: "100 cc. of the water are put into a flask with 3 cc. of a strong

[1] *N. Rep. Pharm.*, **10**, 1.
[2] This Journal, **23**, 405 (1901).
[3] *Chem. News*, **70**, 104 (1894); *Analyst.* **22**, 312 (1897).
[4] "Volumetric Analysis," 7th edition, 1896, p. 96.

solution of calcium or barium chloride, and 2 cc. of saturated solution of ammonium chloride; 45 cc. of baryta or lime-water, the strength of which is previously ascertained by means of decinormal acid, are then added, the flask well corked and put aside to settle; when the precipitate is fully subsided, take out 50 cc. of the clear liquid with a pipette, and let this be titrated with decinormal acid. The quantity required must be multiplied by 3 for the total baryta or lime-water, there being only 50 cc. taken; the number of cubic centimeters so found must be deducted from the quantity required for the baryta solution added; the remainder multiplied by 0.0022 will give the weight of carbonic acid existing as free and as bicarbonate in the 100 cc. The addition of the barium or calcium chloride, and the ammonium chloride is made to prevent any irregularity which might arise from alkaline carbonates or sulphates or from magnesia."

The reactions which take place between the barium and ammonium chorides and magnesium are fully explained in Fresenius' "Quantitative Analysis,"[1] and will not be repeated here.

There are a great many precautions which must be observed in order to obtain results that are at all reliable. Among the principal of these are the avoidance of exposure to the air of the barium hydroxide solution and of the sample of water at all times especially during the titration, the use of a siphon to introduce the sample of water into the ground glass-stoppered bottle in which the precipitation is made, the addition of ammonium chloride during the standardization of the barium hydroxide solution, if rosolic acid is used as an indicator, and the allowance of a sufficient time for the separation of the carbonates in crystalline form before withdrawing the supernatant liquid for titration.

In carrying out this method according to the above directions, even with a strict observance of all the precautions noted, there are several sources of considerable error that do not seem to be generally recognized. They are due to the fact that working on such a small quantity of water as 100 cc. and employing N/10 acid, very slight errors in the titration of the aliquot portion of 50 cc., in measuring out the sample for titration and in measuring the original sample, make a considerable difference in the final result.

Long practice with the method has convinced us that it is impossible to titrate much closer than 0.05 cc., due principally to the

[1] Fresenius' "Quantitative Analysis," English edition, 1889. p. 405.

fact that the best indicator that we can use, rosolic acid, is somewhat affected by ammonium salts, and the end-point is a little uncertain. Suppose, for example, that our barium hydroxide is exactly N/10, 45 cc. equaling 45 cc. of our sulphuric acid, that our measurements are correct, and that after carrying out the process according to Sutton's directions we obtain a reading of 14.40 cc. acid for the aliquot portion of 50 cc. which we titrate. A simple calculation shows this to be equivalent to 3.96 parts per 100,000 carbonic acid in the original sample. Suppose that instead of 14.40 cc. our acid reading had been 14.35 cc.; then a similar calculation shows this to be equivalent to 4.29 parts, as against 3.96 in the first case. This is not only an error of 8.3 per cent. on the value 3.96, but is an absolute difference of 0.33 part on any value, due to this one source of error.

In order to lessen the effect of all three of these errors, we have modified the details of the method as follows:

Ground glass-stoppered bottles of 16-ounce capacity, holding approximately 480 cc., are accurately calibrated by weighing completely filled with water. The bottle is filled with the water to be analyzed by means of a siphon, the glass stopper inserted leaving no air bubble, and the neck of the bottle wiped dry. The glass stopper is then carefully removed, and 57 cc. of the water withdrawn by means of an accurately calibrated pipette, in order to make room for the reagents. Three cc. of strong barium chloride solution (8 grams per liter), 2 cc. of saturated ammonium chloride solution, and 50 cc. of standard barium hydroxide are then introduced, the bottle quickly stoppered, well shaken, and set aside to settle.

There is now in the bottle an air space of only 2 cc., which is left to avoid the possibility of loss of liquid when the stopper is inserted. After the precipitated carbonates have completely settled out, several portions of 100 cc. are siphoned off and titrated with N/50 sulphuric acid, which is prepared from our N/10 acid, against which the barium hydroxide is standardized, by carefully diluting with water freed from carbonic acid by boiling. The barium hydroxide that we use is approximately N/15, and is carefully preserved out of contact with the air, the bottle in which it is kept being fitted with an arrangement whereby the air is drawn through soda-lime before entering either the bottle or the burette. The figure obtained by averaging several results of titration of portions of 100 cc. is taken as the true value.

The use of this large quantity of water and the titration of 100-cc. portions reduce considerably the errors due to the difficulty of obtaining the exact end-point, and those due to inaccuracies of measurement.

The decrease in the concentration of the barium hydroxide solution, due to the increase in the volume of our sample, renders it necessary, in some cases, to allow a longer time than is usually given for the complete precipitation of the carbonates. Standard solutions of free or of combined carbonic acid seem to settle out well on standing over night (that is, twelve to sixteen hours), but some natural waters require longer. We have generally found that samples made up in the afternoon of one day and titrated in the morning of the second day after, have stood a sufficiently long time.

The following table shows one of many series of results obtained by our method with standard solutions of sodium carbonate half neutralized with sulphuric acid.

CARBONIC ACID. (Parts per 100,000.)

Taken.	Found.	Average.	Error. Per cent.
1.10	0.99		
1.10	1.05	1.05	4.5
1.10	1.06		
1.10	1.08		
2.20	1.98		
2.20	2.15	2.14	2.7
2.20	2.23		
2.20	2.20		
3.30	3.12	3.17	4.0
3.30	3.21		
4.40	4.21		
4.40	4.15	4.22	4.0
4.40	4.23		
4.40	4.28		

These samples all stood twenty-four hours before titrating, and the carbonic acid was all in the half-combined state. A great many experiments were also performed in which the sodium carbonate was completely neutralized by sulphuric acid, thus giving all the carbonic acid in the free state. These results were invariably lower than the results on half-bound, due undoubtedly to loss of free carbonic acid during manipulation.

In order to see if more complete precipitation could be ob-

tained by allowing the samples to stand a longer time, the following series of determinations was made:

CARBONIC ACID. (Parts per 100,000.)

Time stood. Hours.	Taken.	Found.
18	2.20	2.25
66	2.20	2.16
113	2.20	2.07
	Average,	2.16

It is seen that the shortest period of the three gave complete precipitation, thus showing that the cause of low results in our first table was not because of insufficient time allowed for the carbonates to separate out.

The following table shows a series of determinations of carbonic acid in natural waters, and in the same waters after the addition of known amounts of carbonic acid (as half-bound).[1]

(Parts per 100,000.)

Water No.	CO_2 added.	Total found.	Mean.	Parts added found.
1	0.00	1.15	1.21	2.31
	0.00	1.27		
	2.20	3.51	3.52	
	2.20	3.52		
2	0.00	1.43	1.51	2.08
	0.00	1.58		
	2.20	3.61	3.59	
	2.20	3.56		
3	0.00	1.32	1.27	2.27
	0.00	1.21		
	2.20	3.54	3.54	
	2.20	3.54		
			Average,	2.22

SEPARATION OF FREE FROM HALF-BOUND.

In order to separate the free from the half-bound carbonic acid, Dr. T. M. Drown has devised the following apparatus: A piece of glass tubing about 2.5 feet long and ⅝ of an inch in diameter, drawn out at one end to a small aperture, is inserted through a rubber stopper into the mouth of an aspirator bottle having a side tubular. The glass tube is filled with gravel about the size of peas. A strong current of air is drawn down through the gravel by means of an aspirator or pump, while the water is slowly dropped

[1] Half-bound added instead of free in order to avoid loss of free carbonic acid in making up solutions.

into the tube at the top from a separatory funnel at the rate of about two drops a second. The water collects in the bottle, and when in sufficient quantity is withdrawn, and the half-bound carbonic acid determined by the Pettenkofer method as before. By this means the free carbonic acid is eliminated from the water, while the half-bound is unaffected. If the water is very high in free carbonic acid, it might be necessary to pass it through the column a second time, but for most waters once is sufficient. The loss in volume due to evaporation has been found to be only about 1 per cent., with a vacuum of 2.5 pounds, and may be neglected in most instances. The following table shows a series of results on standard solutions made by wholly or partially neutralizing solutions of sodium carbonate with sulphuric acid.

SEPARATION OF FREE FROM HALF-BOUND CO_2. (Parts per 100,000.)

Taken.		Found.		
Free.	Half-bound.	Half-bound.	Mean.	Remarks.
4.40	2.20	2.22	2.25	Aspirated 2 drops per second.
4.40	2.20	2.27		" 2 " " "
4.40	2.20	2.31	2.30	" 1 drop " "
4.40	2.20	2.28		" 1 " " "
4.40	2.20	2.17	2.18	" twice, 2 drops per second.
4.40	2.20	2.19		" " 2 " " "
1.10	1.67	1.90	1.84	" 2 drops per second.
1.10	1.67	1.77		" 2 " " "
0.00	2.20	2 31	2.31	" 2 " " "
0.00	2.20	2.30		" 2 " " "
1.10	1.10	1.22	1.22	" 2 " " "
1.10	1.10	1.21		" 2 " " "
2.20	1.10	1.05	1.12	" 2 " " "
2.20	1.10	1.19		" 2 " " "
2.20	2.20	2.36	2.34	" 2 " " "
2.20	2.20	2.31		" 2 " " "

Care must be taken to keep the water dropping at a uniformly slow rate, and to keep the current of air drawing steadily through the tube. If the free carbonic acid is not all expelled, then, of course, the half-bound result is high, and the figure for free, being obtained by subtracting the half-bound from the sum, is naturally low. With careful work, however, the method gives very good results, and is more convenient than the modification of the Pettenkofer method introduced by Trillich in order to accomplish the separation of the free from the half-bound.

THE LUNGE-TRILLICH OR SEYLER METHOD.

This method is very completely discussed in the paper by Ellms and Beneker, and is recommended by them as preferable to any other volumetric method for the determination of free and half-bound carbonic acid in natural water. It depends upon the assumption that in the bicarbonates of the alkaline earth bases there is 1 molecule of half-bound carbonic acid for each molecule of fixed, and that these bicarbonates are neutral to phenolphthalein.

When a solution containing free carbonic acid is titrated with sodium carbonate, with phenolphthalein present as an indicator, sodium bicarbonate is formed; this being neutral to phenolphthalein, as soon as all the free carbonic acid is used up, any further addition of sodium carbonate produces a pink color. Thus the free carbonic acid is obtained directly. By a determination of the fixed carbonic acid by Hehner's[1] process, the half-bound is obtained, as we have assumed this to equal the fixed when the water is acid to phenolphthalein.

When the water is alkaline to phenolphthalein, the phenolphthalein alkalinity is first determined, and then the total alkalinity with lacmoid or methyl orange, according to Hehner's process. Twice the phenolphthalein alkalinity subtracted from the total alkalinity gives the half-bound carbonic acid, no free acid being present in this case, and the half-bound being less than the fixed—that is, some of the normal carbonates are held in solution without the aid of any half-bound.

If no free carbonic acid is present, the half-bound may equal the fixed, and the water will be neutral to phenolphthalein. There is another condition in which carbonic acid might occur in a free state which is mentioned by Seyler, but which would occur so rarely in a natural water that it is hardly necessary to consider.

The mode of procedure is as follows: For the determination of the free carbonic acid, 100 cc. of the sample are introduced into a tall glass cylinder (a 100 cc. nitrite tube) by means of a siphon, 5 or 6 drops of a neutral alcohol solution of phenolphthalein of the usual strength added, and N/50 sodium carbonate run in from a burette with careful stirring, until a permanent faint pink color is obtained. If the water is high in free carbonic acid, it is better to take less than 100 cc., and in any case, great care must be exercised in manipulation, especially in not stirring too

[1] Ellms : This Journal, **21**, 359 (1899).

vigorously, in order to avoid loss of carbonic acid; on the other hand, the titration should be quickly completed in order to avoid absorption of carbonic acid from the air, which readily takes place during the end of the reaction. Great care is necessary in the standardization of the solutions and in their preservation, in order to avoid absorption of carbonic acid.

For the determination of the fixed carbonic acid, from which the half-bound is calculated, the well-known method of Hehner is employed. The writers prefer methyl orange as an indicator.

The following table shows the action of sodium carbonate solutions with the two indicators, when titrated with sulphuric acid.

Solution No. 1.			Solution No. 2.		
	cc H_2SO_4.			cc. H_2SO_4.	
cc. Na_2CO_3.	Methyl orange.	Phenol-phthalein.	cc. Na_2CO_3.	Methyl orange.	Phenol-phthalein.
10	9.75	4.85	10	9.65	4.78
10	9.67	4.90	10	9.62	4.80
10	9.73	4.85	10	9.63	4.80
10	9.70	4.84	..	...	...
10	9.75	4.89	..	...	...
Average,	9.72	4.87		9.63	4.80

With phenolphthalein as an indicator, only half the quantity of acid is required to give an end-point as with methyl orange.

THE DIRECT METHOD.

This method for the determination of carbonic acid consists in boiling off the gas in a suitable apparatus, fitted with a return-flow condenser and drying tubes, and absorbing the carbonic acid in a weighed potash bulb or soda-lime tube. Various modifications of the apparatus have been employed by different workers, but the form that we have found quite satisfactory is constructed as follows: A liter, round-bottomed flask, supported on a lamp-stand, contains the sample of water, and a perforated rubber stopper fits tightly into the neck of this flask. Through one perforation passes a return-flow condenser, while through the other passes a tube bent so as to form a water-seal, and carrying at its upper end a small separatory funnel.

The return-flow condenser is a tube about 24 inches long and 0.5 inch in diameter for 7 inches of the lower end and 5 inches of the upper end, while the main body of the tube is 1 inch in diameter, and is surrounded by a water-jacket. This form of tube is employed in order to give a large condensing surface.

A small delivery tube conducts the carbonic acid gas through a U-tube containing glass beads moistened with sulphuric acid, thence through another U-tube containing fused calcium chloride, thence to the potash bulb. Beyond the potash bulb is a tube containing soda-lime, to remove carbonic acid from any air accidentally drawn back into the bulb during the process.

Before each analysis the apparatus is freed from carbonic acid by boiling water in the flask, and aspirating while cooling, until the bulb weighs constant. When the flame is removed, an aspirator is attached to the last tube, in order to draw through any carbonic acid which may be present, and to equalize the pressure before disconnecting the bulb. All the air which enters the apparatus is drawn through a Liebig bulb containing caustic potash solution and connected with the separatory funnel.

The free and half-bound carbonic acid are thus determined together in this apparatus. In order to differentiate, the fixed may be decomposed by sulphuric acid introduced by means of the separatory funnel after the free and half-bound are expelled, and the carbonic acid evolved absorbed in the weighed bulb as before.

From these data, the half-bound acid may be calculated.

The following table shows a few results by this method on standard solutions. In order to avoid loss of carbonic acid, they were prepared by measuring into the flask the required amount of dilute sulphuric acid, then introducing the weighed amount of sodium carbonate wrapped in a bit of paper. Before the reaction could take place, the flask was quickly stoppered.

CARBONIC ACID. (Parts per 100,000.)

Taken.			Found.		
Free.	Half-bound.	Sum.	Free.	Half-bound.	Sum.
3.30	...	...	3.20	...	...
4.40	...	...	4.47	...	...
4.40	...	...	4.40	...	...
4.40	...	...	4.40	...	...
2.93	1.47	4.40	...	...	4.30
3.23	0.59	3.82	...	...	3.60
1.47	1.47	2.94	1.47[1]	1.20	2.67
2.93	1.47	4.40	3.07[1]	1.13	4.20
1.47	1.47	2.94	1.73[1]	1.27	3.00
5.87	2.93	8.80	...	...	8.53
5.87	2.93	8.80	...	3.00	...

[1] In every case the sum of the free and the half-bound acid is determined first, and then the fixed, from which the half-bound is calculated. The free is thus always obtained by difference, and any error in either the sum or the half-bound affects the free result; in fact, these errors are frequently in the same direction, so that the accuracy of the free result is not as great as that of the other figures.

These results show the method to be capable of giving fairly accurate results, on standard solutions, at least, especially when the carbonic acid is all in the free state. When there is half-bound also present, it is somewhat more difficult to obtain accurate results, the tendency being for them to be low on account of the difficulty of expelling the last traces of half-bound carbonic acid. A source of some trouble in the method when a potash bulb is used is the tendency of the potash solution to go over into the drying tube, due to the strong suction which it is necessary to apply in order to keep the current moving always in the right direction.

In working with natural waters, this method has been applied only to clear and colorless waters containing little organic matter, as according to some writers, in some waters, especially those which are polluted with sewage,[1] decomposition of unstable organic matter at the boiling temperature may liberate free carbonic acid.

COMPARATIVE DETERMINATIONS BY ALL THREE METHODS ON NATURAL WATERS.

In experiments on standard solutions with various methods of determining carbonic acid, the conditions are quite different from those obtained in actual practice, as it is impossible to prepare the standard solutions so that they are similar in composition to natural waters, since the composition of the natural waters in which we are called upon to determine carbonic acid varies greatly. For this reason a series of results obtained by any method, in solutions of carbonic acid in distilled water does not necessarily determine to what degree of accuracy the method may be relied upon in actual practice. This is especially true of the Seyler method, as the titration of solutions of carbonic acid made by partially or completely neutralizing sodium carbonate solutions with sulphuric acid amounts to little more than a restandardization of the solutions. The errors that are found in such results are the errors of standardization and of manipulation in making up the solutions. Also, in both the Pettenkofer and the Seyler methods the principal cause of low results on free carbonic acid is due to the loss which unavoidably occurs before the method can be fairly applied.

The following table shows a series of determinations on natural waters of varying composition:

[1] Burghardt: *Chem. News*, 1887, p. 121.

CARBONIC ACID. (Parts per 100,000.)

Water No.	Seyler.			Modified Pettenkofer.[1]			Direct boiling.
	Free.	Half-bound.	Sum.	Free.	Half-bound.	Sum.	Sum.
1	1.98	0.57	2.55	...	...	2.60	2.53
2	2.02	0.62	2.64	1.90	0.69	2.59	2.40
3	0.75	0.70	1.45	...	...	1.25	...
4	1.01	0.57	1.58	0.21	0.48	0.69	1.47
5	1.10	1.32	2.42	...	...	1.92	2.67
6	0.79	0.53	1.32	...	...	1.13	1.20
7	0.97	1.10	2.07	1.05	1.19	2.24	...
8	0.70	0.97	1.67	0.84	0.70	1.54	...
9	1.76	1.28	3.04	1.84	1.34	3.18	...
10	0.57	1.23	1.80	0.77	1.07	1.84	...
11	0.26	0.26	0.52	0.13	0.44	0.57	...
12	2.20	0.44	2.64	2.19	0.61	2.80	...
13	0.57	0.26	0.83	0.51	0.33	0.84	...
14	0.75	0.53	1.28	0.32	0.77	1.09	...
15	0.75	1.85	2.60	0.99	1.57	2.56	...
16	0.92	1.45	2.37	0.88	1.18	2.06	...
17	0.84	1.32	2.16	0.93	1.02	1.95	...
18	0.26	0.40	0.66	0.15	0.34	0.49	..
19	0.70	0.31	1.01	0.45	0.28	0.73	...
20	0.04	1.41	1.45	0.11	0.83	0.94	...
21	0.88	1.06	1.94	1.00	0.64	1.64	. .
22	0.97	0.66	1.63	1.18	0.24	1.42	...
23	2.64	0.48	3.12	0.91	0.31	1.22	...
24	0.62	0.70	1.32	0.65	0.20	0.85	...
25	2.29	1.45	3.74	...	...	3.66	...
26	2.86	0.31	3.17	...	...	1.85	...
27	1.94	1.01	2.95	...	...	2.36	...
28	1.94	0.92	2.86	...	...	2.87	...

It is a rather difficult matter to make comparisons of the two principal methods, the Seyler and Pettenkofer, for the following reasons: All the waters were acid to phenolphthalein and so by the Seyler method the free carbonic acid was phenolphthalein and so by the Seyler method the free acid was determined directly, and the half-bound calculated from the fixed, which is determined by Hehner's method. Thus, the free and the half-bound represent actual determinations, while the sum is naturally obtained by adding these two results together. In our modification of the Pettenkofer method, on the other hand, the sum and the half-bound represent actual determinations, while the free is obtained by difference. It is thus seen that the only one of

[1] Free expelled by aspirating, and the half-bound determined; this figure subtracted from the sum to give the free.

the three figures which represents an actual determination in both methods is the figure for half-bound; and unfortunately, in one method, the Seyler, this figure is obtained independently of the free, while in our modification of the Pettenkofer method this figure is dependent on the thoroughness with which the free is expelled by aspiration.

A study of the table shows the following facts:

1. In seven out of twenty cases in which complete results were obtained by both methods, no result by either method differs from the corresponding result by the other method by over 0.20 of a part. This is a large percentage difference, to be sure, when the figure is low, but is a small absolute difference when the opportunities for error are considered, and as far as our present knowledge of the significance of carbonic acid in a drinking-water goes, such small differences are not important.

2. Considering only the half-bound results, as these figures are more nearly comparable in both methods, it is seen that in thirteen out of twenty cases, in which the half-bound was determined, the Seyler result is higher than the modified Pettenkofer. This seems to indicate that the method of separation of the free from the half-bound by aspiration in the modified Pettenkofer method can be relied upon for sufficient accuracy.

3. Considering the figures for the sum of the free and half-bound obtained by both methods, it is seen that in twenty instances out of twenty-eight in which the sum was determined, the result by the Seyler method was higher than that by the modified Pettenkofer. In experiments Nos. 1, 2 and 6, the results on the sum of the free and half-bound by three methods vary less than 0.10 part from the average of the three figures.

4. Considering the free results, it is seen that out of twenty determinations, the Seyler method gave higher results in ten, or just half.

From these few comparisons it appears that the Seyler method tends to give higher results than the modified Pettenkofer, and that these higher results are nearer the true value is shown by the results obtained by the boiling method, and also by the experiments on standard solutions.

To know the amount of the carbonic acid that is in the free state is of the most importance to the water analyst, so it is the result on the free acid that really deserves the most attention.

It will be seen from the table that, although half the free results by the modified Pettenkofer method are higher than those by the Seyler, yet there are some results which are erratic. For example, in experiment No. 4, the sum by the Seyler method checks well with the result obtained by the boiling method, and the results on half-bound by both the Seyler and the modified Pettenkofer methods agree well, yet the sum, and hence the free which depends upon it, is much lower in the modified Pettenkofer than in the Seyler. This is only one example among many similar ones which have occurred and which we have not given in our table.

The cause of these erratic results which frequently occur in the Pettenkofer method is not apparent from any of our experiments. It is a well-known fact that magnesium is liable to influence the results somewhat, but whatever might be learned by experiments with standard solutions containing magnesium, our experience has shown that the erratic results frequently obtained by this method with natural waters cannot often be traced directly to this element.

Considering the experiments of other investigators, together with those which we have performed, it seems that there is something to be said in favor of each method. Both methods require the utmost care in manipulation, this being especially true of the Seyler method for the determination of free carbonic acid. The advantages of the Pettenkofer method seem to be the less liability to loss or absorption from the air of free carbonic acid during the determination of the sum or half-bound, while the longer time and more apparatus required to complete the determination constitute a disadvantage. In regard to accuracy, the results are generally somewhat low, especially with waters low in carbonic acid, and frequent erratic results are obtained. The presence of magnesium salts is also a possible source of difficulty.

The Seyler method has the advantage of convenience and quickness of execution, but the determination of the free carbonic acid by titration with phenolphthalein as an indicator is a matter of considerable uncertainty, and under some conditions, of difficulty. Disturbances due to the presence of magnesium salts are avoided in this method, and the determination by Hehner's method of the fixed, from which the half-bound is calculated, is satisfactory. The results by this method are liable to be somwhat low, but not as low as those by the Pettenkofer.

Neither method can be relied upon to give results always within

a certain percentage of the true values, and thus neither has a preeminent claim to scientific accuracy; for practical work in water analysis, however, the Seyler method, in the hands of an experienced operator, especially on account of rapidity of completion, has much to commend itself, and it is our purpose to employ it in our regular work.

MASSACHUSETTS STATE BOARD OF HEALTH,
LABORATORY FOR WATER ANALYSIS, BOSTON, MASS.

TITRATIONS WITH POTASSIUM IODATE.

BY LAUNCELOT W. ANDREWS.

Received May 23, 1903.

As is well known, when potassium iodide is titrated with chlorine water in a neutral solution, the reaction which takes place is expressed by the equation:

$$KI + 3Cl_2 + 3H_2O = KCl + HIO_3 + 5HCl. \qquad (1)$$

On the other hand it may not be so well known that if a large excess of free hydrochloric acid is present during the titration, chloroform or carbon tetrachloride being used as before for an indicator, the reaction will be

$$KI + Cl_2 = KCl + ICl. \qquad (2)$$

In both cases the end of the reaction is shown by the immiscible solvent becoming colorless. If instead of chlorine water we titrate with a solution of potassium iodate, the stage at which the reaction stops is likewise dependent upon the concentration of the acid. If this be low, the reaction goes no further than to set the iodine free in accordance with the equation

$$5KI + KIO_3 + 6HCl = 6KCl + 3I_2 + 3H_2O, \qquad (3)$$

while if a great excess of hydrochloric acid is present the reaction runs

$$2KI + KIO_3 + 6HCl = 3KCl + 3ICl + 3H_2O, \qquad (4)$$

the immiscible solvent remaining violet in the former case (No. 3), but in the latter becoming colorless, while the supernatant solution turns bright yellow from the iodine chloride. The probable explanation of this behavior is that iodine chloride, as the salt of a very weak base, undergoes hydrolysis in a neutral or feebly acid solution, with the production of the corresponding hydroxide and acid; thus,

$$ICl + H_2O = IOH + HCl, \qquad (5)$$

the iodous hydroxide ("hypoiodous acid"), which is formed, undergoing spontaneous conversion into iodic acid, etc., whereas the hydrolysis is prevented by a great excess of hydrochloric acid.

The reaction of equation (1) was used long ago by A. and F. Dupré[1] for the titration of iodides. In order to compare the reactions of the first two equations, I titrated 5 cc. of a decinormal potassium iodide solution with chlorine water in presence of 5 cc. of chloroform. After the addition of 75.4 cc. of the latter the chloroform became colorless. The titration was now repeated with the further addition of respectively 15, 20 and 30 cc. of strongest hydrochloric acid and the amounts of chorine water required were, 25.4, 25.22 and 25.25 cc., the end reaction being of extraordinary sharpness. Nearly three times as much chlorine was, therefore, required in the absence of hydrochloric acid as in its presence, as the theory demands. Probably, if the small amount of acid produced by the reaction itself (equation 1) had been neutralized by the addition of calcium carbonate, the theoretical amount of 75.75 cc. of chlorine solution would have been required. In order to judge the influence of smaller quantities of acid, the titration was repeated with addition of 1, 2, 5 and 10 cc. of concentrated hydrochloric acid, when respectively 34.1, 26.9, 26.0 and 25.6 cc. of chlorine water were required.

From these preliminary experiments, it appeared that the hydrolysis of the iodine chloride might be wholly inhibited by addition of a sufficiency of acid and that a solution of potassium iodate might be successfully substituted for the chlorine water, thus realizing the reaction of equation 4. 9.7465 grams of acid potassium iodate were dissolved in water and made up to 1 liter. According to the theory, each cubic centimeter of this solution should be equivalent to 16.6 mg. of potassium iodide. To 10 cc. of a solution of pure potassium iodide (20.6 grams to the liter), 5 cc. of chloroform, 20 cc. of water and 30 cc. of concentrated hydrochloric acid (sp. gr. 1.21) were added and the mixture was titrated in a glass-stoppered bottle of 250 cc. capacity, with the iodate solution, shaking briskly, until the chloroform lost its color, the end-point being exceedingly sharp. 12.43 cc. of the iodate solution were required. Hence, 0.20634 gram potassium iodide was found against 0.20600 taken, or 100.17 per cent. In a second ex-

[1] *Ann. Chem.* (Liebig), **94**, 365 (1855).

periment, 15 cc. of the iodide solution titrated in the same way with 33 cc. of hydrochloric acid and no additional water, required 18.62 cc. of the iodate solution, corresponding to 0.30900 gram found, against 0.30900 gram taken, or 100.00 per cent., found.

The process as described can be applied to the titration of chromates. For this purpose the chromate is added to an excess of a titrated potassium iodide solution, with 5 cc. of chloroform and sufficient concentrated hydrochloric acid to be at least half the volume of the entire mixture at the close of the titration. The titration is then carried out precisely as described above. In one experiment of this sort, 36.3 mg. of potassium pyrochromate were taken and 36.8 mg. found.

The following experiment shows the applicability of the process to the titration of free iodine: 0.3447 gram of pure iodine was weighed and placed in the stoppered bottle previously used, with 5 cc. of a potassium iodide solution containing 20.6 grams per liter, 10 cc. of fuming hydrochloric acid and 5 cc. of chloroform were added, and the titration was carried out in the usual way. Required: 19.85 cc. of standard iodate. Since 6.20 cc. are required for the iodide, 13.65 cc. remain as corresponding to the free iodine, or 0.3467 gram iodine found; 100.46 per cent.

To determine whether the method can be used for determination of chlorates, and under what conditions, the succeeding experiments were tried. Five cc. of a solution of potassium chlorate containing 70.3 mg. of the pure salt was added to 25 cc. of the potassium iodide solution mentioned above and 50 cc. of fuming hydrochloric acid. After standing fifteen minutes in the stoppered bottle, 5 cc. of chloroform were added and the titration completed. Required: 13.65 cc. of the iodate. As the iodide is equivalent to 31.0 cc., 17.35 cc. correspond to the chlorate, whence 70.9 mg. of potassium chlorate were found. In a second similar experiment only 40 cc. of hydrochloric acid were used, and the mixture was titrated at once, without standing. In this case 13.98 cc. of iodate were required, hence 69.55 mg. of chlorate were found. This shows, as was expected, that the chlorate must be left for some time in contact with the hydrochloric acid and potassium iodide for the completion of the reaction. In a third experiment exactly similar to the last except that the mixture was allowed to stand twenty-four hours before titration, 13.77 cc. of iodate were required, whence 70.41 mg. of chlorate were found.

It is therefore a matter of indifference whether the time of digestion is a quarter of an hour or twenty-four hours. In a fourth experiment, 5 cc. of another potassium chlorate solution containing 33.46 mg. of the pure salt was allowed to stand for ten minutes with 10 cc. of iodide solution and 20 cc. of fuming hydrochloric acid, then 5 cc. of chloroform were added, and the titration was performed. Required: 4.23 cc. of iodate. Calculated for the iodide, 12.40 cc., whence 33.39 mg. of chlorate were found. Other experiments, not necessary to detail, show that there must be a decided excess of iodide as compared with the chlorate; otherwise the results are likely to be a little too low. The necessary working conditions for the titration of a chlorate can be prescribed as follows.

To the solution of the chlorate, add an exactly known amount of pure potassium iodide (a titrated solution may be used), in a glass-stoppered bottle, and an amount of fuming, pure hydrochloric acid at least one-third greater than the volume of the solution. Close the bottle tightly and allow it to stand fifteen minutes after shaking, then add 5 cc. of chloroform. On now shaking, the chloroform must become deep violet. If the color is pale, an insufficiency of iodide has been added, and it is better to begin again rather than to attempt to bring the analysis into order. Now add the decinormal iodate with intermittent violent shaking until the chloroform becomes colorless, which point can be estimated with the utmost precision. Each cubic centimeter of a decinormal iodate solution is equivalent to 2.782 mg. of $(ClO_3)'$.

Solutions of arsenious acid or chloride can be titrated in the same way as iodides, the reaction being expressed by the equation

$$2AsCl_3 + KIO_3 + 5H_2O = 2H_3AsO_4 + KCl + ICl + 4HCl.$$

In this case, however, unlike the other, a too great concentration of hydrochloric acid must be avoided, since under those conditions the end-point becomes obscure, probably a phenomenon connected with the formation and dissociation of arsenic pentachloride. The suitable concentration of the acid is therefore confined within somewhat narrow limits, but not so narrow as to cause any practical difficulty in working. It was found that 30 per cent. of hydrochloric acid, calculated on the weight of the entire liquid at the close of the titration, exceeds the permissible maximum limit, while 25 per cent. does not. On the other hand, the minimum limit is in

theneighborhood of 12 to 15 per cent. of acid. For the experiments noted below, a solution of sodium arsenite was employed in which the amount of arsenious oxide had been determined by titration with iodine solution in the ordinary way. Taken: 25 cc. arsenious solution (243.8 mg. As_2O_3) and 50 cc. of fuming hydrochloric acid. Required: 24.45 cc. decinormal=242.1 mg. of arsenious oxide. Taken:5 cc. arsenious solution, 5 cc. hydrochloric acid, and 10 cc. water. Required: 4.91 cc. of iodate = 48.6 mg. Found: 48.8 mg. by iodine titration. Taken: 20 cc. arsenious solution and 40 cc. hydrochloric acid. Required: 19.69 cc. iodate = 194.9 mg. arsenious oxide. Found: 194.7 mg. by iodine titration. Taken: 15 cc. arsenious solution and 30 cc. hydrochloric acid. Required: 14.79 cc. iodate = 146.4 mg. arsenious oxide. Found: 146.3 mg. by iodine titration.

To summarize: Add to the arsenious solution an amount of fuming hydrochloric acid sufficient to make the hydrochloric acid equal to about 20 per cent. of the entire mixture at the end of the titration, and 5 cc. of chloroform; then run in from a burette as large a proportion as can be judged of the whole amount of decinormal iodate requisite, shake well and continue titrating with the iodate until the chloroform is colorless. Each cubic centimeter of the standard solution corresponds to 9.9 mg. arsenious acid or 7.5 mg. arsenic.

The determination of antimony is precisely like that of arsenic. A solution was prepared of pure recrystallized potassium antimonyl tartrate, containing 31.251 grams per liter. Twenty-five cc. of this were mixed with 30 cc. hydrochloric acid and 20 cc. water, and titrated as usual. 23.62 cc. of the iodate were required, equivalent to 784.6 mg. tarter emetic found as against 781.3 mg. taken. In this determination the amount of hydrochloric acid should have been greater by 15 cc. In the next experiment, 25 cc. of the antimonious solution with 25 cc. of hydrochloric acid required 23.50 cc. of iodate, equivalent to 780.6 mg. of antimony salt found (781.3 taken). Twenty-five cc. antimony solution with 35 cc. fuming hydrochloric acid required 23.54 cc. of iodate, whence is calculated 781.2 mg. potassium antimonyl tartrate.

Since copper does not interfere in the least with the application of the method, it is possible, for example, to titrate the arsenic in Paris green directly without preliminary separation. Thus, 20 cc. of a sodium arsenite solution with 20 cc. of fuming hydro-

chloric acid required 8.95 cc. of iodate; the same, plus 1 gram of copper sulphate, required 9.00 cc. of iodate. For the analysis of Paris green, 0.5 gram of the substance is dissolved in 15 cc. of water and 25 cc. of fuming hydrochloric acid, and directly titrated with 5 cc. of chloroform and the decinormal solution of iodate.

Ferrous salts can be titrated in exactly the same way as iodides. Taken: 2.0874 grams ammonium ferrous sulphate. Required: 26.06 cc. iodate, equivalent to 297.6 mg. iron found, or 14.26 per cent. Theory: 14.25 per cent. Unlike the titration with potassium permanganate, oxalic acid does not interfere with thisdetermination. Taken: 2.0843 grams ammonium ferrous sulphate and 1 gram oxalic acid. Required: 25.95 cc. iodate, equivalent to 296.3 mg. iron, or 14.22 per cent. Ferric salts do not interfere with any of these titrations, nor do bromides to any serious extent, if the amount is small. The end-reaction in the titration of ferrous salts is somewhat slow and, in spite of the satisfactory results of the test analyses, is lacking in the sharpness that distinguishes the other titrations described in this paper. This difficulty appears to be avoided by the addition of a small amount of manganous chloride, but the point requires further examination.

The method which has been described is adapted to the determination of almost all the substances to which Bunsen's process of distillation with potassium iodide and hydrochloric acid is applicable, with at least equal precision, with less expenditure of time and far simpler apparatus. It is furthermore applicable in certain cases in which the Bunsen method is not, as, for example, the titration of arsenic or antimony in the presence of copper and ferric compounds.

CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA, May 5, 1903.

THE PERMANENT PROTECTION OF IRON AND STEEL.[1]

BY MAXIMILIAN TOCH.

Received April 14, 1903.

The question of the permanence of modern steel structures, whether the iron and steel used therein is slowly corroding and will in time cause great calamity by the collapse of these structures, has led chemists and engineers to make extensive researches into

[1] Read before the New York Section of the American Chemical Society.

the stability of iron and steel exposed to atmospheric influence. Both exposed and embedded iron are subject to progressive oxidation under certain conditions, and evidence of this is offered in the record of many cases of rusting of girders and "I" beams of railroad and other bridges, while manufacturers of paints have long endeavored to make a coating of material which would prevent corrosion and oxidation.

The success of such coatings depends mostly upon the skill of the workmen and their proper application. A good paint improperly applied is relatively as poor as a paint of lesser merit. Red lead, for instance, is condemned as often as commended and it is probable that those who have commended it have had it properly applied by skilful workmen under favorable conditions, and then had it covered by better paint. At the same time, it may be regarded as an axiom that it is a blunder to apply a corrosive oxide to a material that will corrode. If a paint be in itself a carrier of oxygen, and the iron or steel be subjected to the action of alternate dampness or dryness or of air charged with carbon dioxide, progressive oxidation is sure to take place and the tensile strength of the metal to be materially reduced. Such conditions may readily occur when a beam is placed in a porous wall. Rapid and continuous oxidation takes place, if steel or iron which is partly rusted is covered with red lead and left exposed.

About fifteen years ago a pamphlet was published in Germany intended to prove that this oxidation is due to electrolytic action, and while the quantity of electricity involved has not been measured, nor positive evidence of it adduced, it seems plausible that such a condition may exist. An iron bar bedding in stone, packed with metallic lead at the point where it enters the stone, always rusts rapidly, suggesting electrolytic action. When two pieces of steel come in contact in a building, rapid oxidation occurs at the point of contact, and this is particularly true of bolt-heads and grill foundation work.

If a clean, pure, cement concrete is packed hard against an iron or steel surface, little or no oxidation can take place, especially if free lime has been liberated in the setting of the cement; but violent oxidation can take place if cinder concrete containing iron oxide, other metallic oxides, free chlorine or any trace of a sulphide be used.

Pieces of anchor chains, which have been embedded in concrete

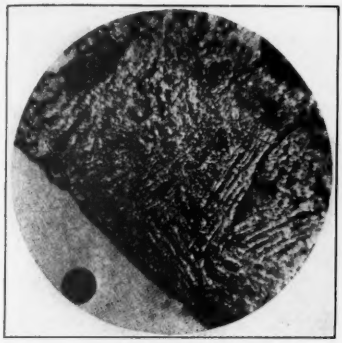


Fig. 1.

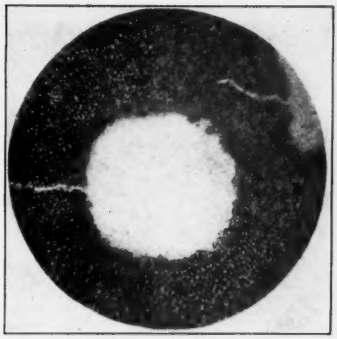


Fig. 2.

Fig. 3.

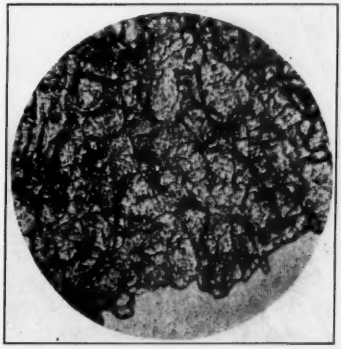


Fig. 4.

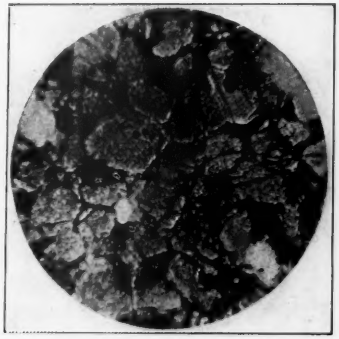


Fig. 6.

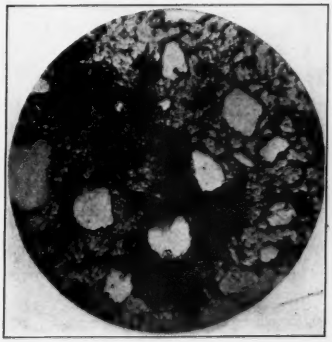


Fig. 7.

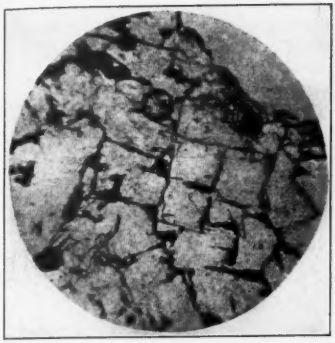


Fig. 8.

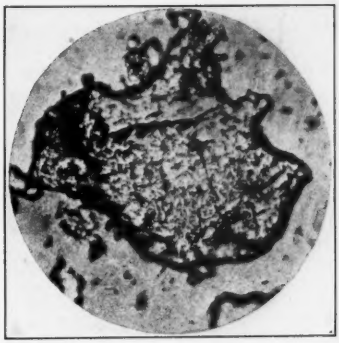


Fig. 9.

Fig. 10.

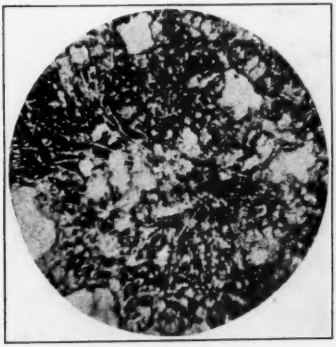


Fig. 11.

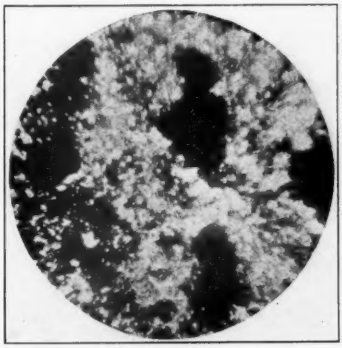


Fig. A.

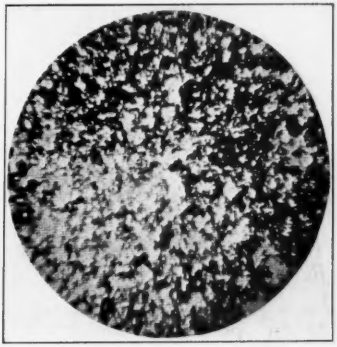


Fig. B.

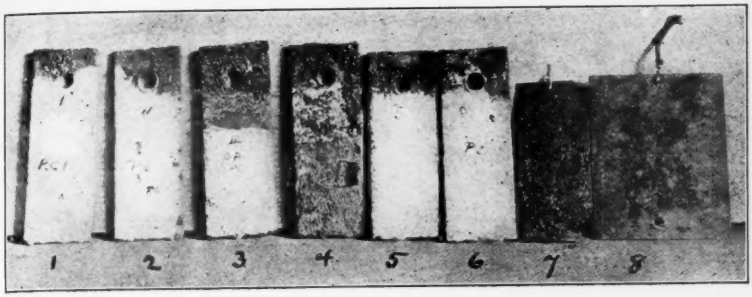


Fig. C.

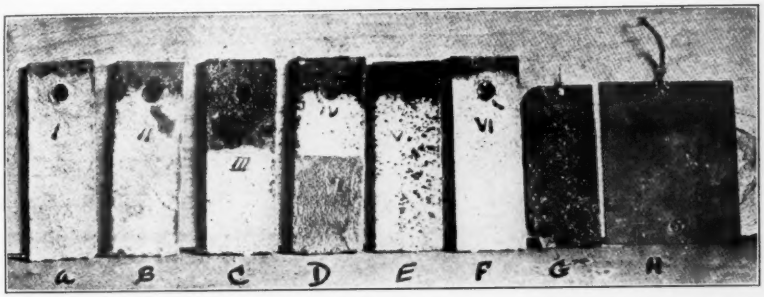


Fig. D.

Fig. E.

more than 200 years, have been found in Spain in a state of perfect preservation. Large quantities of metal unearthed in Italy and Greece, extremely old, embedded in cement or concrete, are wonderfully well preserved. These and other observations led me to experiment with Portland cement for the protection of iron and steel against oxidation.

Portland cement, prepared from pure materials in molecular proportions, consists of tricalcium silicate and dicalcium aluminate in a state of solid solution and in the proportion of 85 per cent. of $SiO_2.3CaO$ and 15 per cent. of $Al_2O_3.2CaO$. A Portland cement may also exist in which the aluminate is replaced by dicalcium ferrite, $Fe_2O_3.2CaO$. When such a cement is treated with water, it is decomposed, hydration takes place, and hydrated calcium silicate of lower basicity, combined with an alumina or iron compound, is formed and the product is known as *set cement*. Free lime is liberated at the same time and this explains why linseed oil paint applied to newly set cement is ineffective and why a proper mixture of cement over iron precludes oxidation.

I am indebted to Mr. Clifford Richardson for the use of certain thin sections of typical Portland cements and synthetic compounds prepared to illustrate the structure and physical properties of these important substances. I have made photo-micrographs of these sections which have been reproduced in the following illustrations. In the plates

Fig. 1 represents synthetic $SiO_2.3CaO$.

Fig. 2, synthetic $SiO_2.Al_2O_3.6CaO$.

Fig. 3, synthetic $SiO_2.4Al_2O_3.10CaO$.

Fig. 4, Universal Portland cement clinker.

Fig. 6, Portland cement clinker containing 7 per cent. Fe_2O_3 and no Al_2O_3.

Fig. 7, Celite in Portland cement clinker.

Fig. 8, synthetic $2Al_2O_3.3CaO$.

Fig. 9, synthetic $SiO_2.2CaO$.

Fig. 10, tricalcium aluminate, $Al_2O_3.3CaO$.

Fig. 11, Felite rods in Portland cement clinker.

Fig. A, properly treated Portland cement, finely ground and which sets quickly, magnified 100.

Fig. B, best commercial Portland cement, magnified 100, not fit for paint protection.

To confirm the value of Portland cement for the protection of iron and steel, I prepared cement having the composition above

indicated, that is, 85 per cent. of tricalcium silicate and 15 per cent. of dicalcium aluminate, in solid solution with each other. This substance, reduced to fine powder, was mixed with water to a thin paste and applied to plates of steel. The coated plates were subjected to various unfavorable influences, tending to cause them to corrode and rust. About 2 in. of one end of each plate was left uncovered, and this space was in every case badly rusted. When the treatment was completed, the plates were all photographed and the photographs reproduced in the following illustrations.

In the illustrations, Figs. C and D, 1 to 6, and A to F, respectively, represent the same set of plates which were submerged in earth through which was passed, for a period of three months, a current of electricity from a crow foot battery of two cells. The earth was moistened alternately with ammonia, weak nitric acid, and an aqueous solution of ammonium chloride and water. The plates were set in a row, parallel with each other. In the illustrations, Fig. C, 1 to 6 represents the anode sides, and Fig. D, A to F, the cathode sides of the plates.

Fig. 7 represents the plate which was connected with the anode wire and 8, that connected with the cathode wire.

Fig. C, 7, and Fig. D, G show that the anode plate was completely rusted even around the edges, while Fig. C, 8 and Fig. D, H show that the anode plates were much better preserved.

In Fig. C, plate No. 1 was properly treated with pure Portland cement. When removed from the ground it was perfectly preserved and showed no trace of oxidation.

Plate No. 2 was treated with commercial Portland cement containing some metallic iron and calcium sulphate. Marked incrustation of rust appeared under the cement.

Plate No. 3 was coated with an oil paint and afterward covered with cement. It was fairly well protected.

Plate No. 4 was first coated with cement and the latter afterward covered with oil paint. The steel was perfectly preserved.

Plates Nos. 5 and 6 were covered respectively with different samples of Portland cement, the covering of No. 5 being worthless and that of No. 6 excellent.

Fig. E, plates numbered 9 to 17, respectively, were coated with various cement and paint preparations, and subjected to the action of different conditions and reagents. The effect in each case is indicated in the illustration.

Plate No. 9 was coated in the same way as plate No. 1 and for three months was sprinkled with water once a week and allowed to dry. The uncoated portion was badly rusted, but the covered portion was perfectly protected.

Plate No. 10 was coated with cement and an oil paint. Plate No. 11 was coated with cement and a hydrocarbon paint. It was subjected to water and the elements alternately with no unfavorable result.

Plates Nos. 12 and 13 were coated with cement in the same way as plate No. 1 and then supported in a large beaker, the bottom of which was covered with fuming nitric acid. Some of the acid touched the lower end of the plates and lightly corroded them. The uncovered portions were badly corroded, but the acid fumes did not penetrate the cement, and the plates remained in an excellent state of preservation.

Plate No. 13 was subjected for a short time to the influence of fume liberated after addition of hydrochloric acid.

Plate No. 14 was first coated with hydrocarbon oil paint. Subjected during three months to nitric acid fumes, it showed no corrosion under the cement.

Plate No. 15 was prepared in the same way as No. 14 and subjected to the influence of sulphuric acid, carbonic acid and steam; underneath the coating it was thoroughly preserved.

No. 15 is a bar of steel which was coated with a wash of cement of the best commercial grade. The protection was fairly good, but the coating, exposed to wind and rain, was washed off after a few months.

Plate No. 17 was covered first with oil paint and afterward with prepared cement. Roughly handled during eight months, the covering flaked off and the steel was badly corroded.

As a result of the experiments made with the mixture prepared and applied after the manner just described, we may conclude:

(1) If a proper cement paint be applied to a surface which has begun to oxidize, further oxidation will be arrested.

(2) If the cement used be very fine and free from iron, calcium sulphate and sulphides of low specific gravity, it will quickly set on the surface and eventually become thoroughly fixed upon the metal so that rain will not wash it off.

(3) When thoroughly applied, even to three coats, the concrete may be painted with alkali proof and adherent paint, afford-

ing absolute protection to iron so that moisture, carbon dioxide or factory fumes will not penetrate.

(4) Cement paste for application to iron or steel must be made with pure water, and the mixture must be stirred at least fifteen minutes to admit of the liberation of the lime.

(5) Free lime on the surface of the cement coating is quickly carbonated, and then has no injurious action upon linseed oil paint which may, under such conditions, be applied and become extremely efficacious.

The method of waterproofing brick walls from the outside as a protection against penetrating rain or dampness is important in this connection. A newly set brick contains as much as 8 ounces of water, and its power to adhere to the mortar increases with the quantity of water it contains. If a linseed oil paint be applied to a newly erected and wet wall, it quickly peels off and ruins the wall for the further application of paint. But if a proper cement mixture is applied to such a wall in the form of paint or whitewash, it not only adheres perfectly, but forms an excellent base for the application of a good linseed oil paint. Painting the outside wall of a building in this way has some influence on the permanent protection of iron and steel used in construction, since it prevents in a large degree the access of carbonic acid, moisture and gases.

In view of what has just been stated, it is reasonable to believe that structural metal works which have been coated with a layer of cement paint and further protected by a layer of hydrocarbon insulating paint, when embedded in masonry, will be perfectly immune to oxidation and will probably last for all time.

A similar coating affords efficient protection to pipes and conduits placed in the ground and subjected to various influences such as of moist gases, electric currents, acid and alkaline liquids.

Pure Portland cement mixed with water cannot be used as a wash on metal because it will not always set, and it is apt to crack when it does, hence it must be diluted. But care must be exercised that the dilution be not carried too far and the strength of the cement thereby impaired. Voids can be prevented by careful brushing, and for certain structural works where brush work is impracticable, spraying will be effecive, but the cement must then be applied in several layers.

NEW YORK, February 6, 1903.

NOTES.

Note on the Mononitro-o-Phthalic Acids.—Since the publication in this Journal of the article by Bogert and Boroschek[1] upon the mononitro-*o*-phthalic acids, certain facts have come to light which seem to call for a few additional notes from us.

In the first place, we have discovered, among a number of dissertations recently secured by Columbia University, several dealing wholly or in part with the nitrophthalic acids. Two of these, namely, one by Max Levi, submitted to Freiberg (i. B.) University in 1891, the other by Adolph Koch, submitted to the University of Geissen in 1900, antedated part of the work reported by us. So far as we know these results have not been published in any of the chemical journals and do not appear in "Beilstein." Of the derivatives prepared by us, the following are also described in these dissertations.

3-Nitrophthal-1-Amic Acid.—By the action of hydrochloric acid upon the sodium salt of the imide, Levi[2] obtained a crystalline compound to which he assigned the 1-amic acid structure. The acid prepared by us by the action of baryta water upon the imide, and for which we suggested the 2-amic acid constitution, has recently been shown by Kahn[3] to be the 1-amic acid. As Levi did not analyze his product and gives very few data concerning it, it is doubtful whether he really had the pure 1-amic acid in hand, particularly as he reports the substance to be "quite easily" soluble in ether, whereas the 1-amic acid is really very difficultly soluble in ether.

3-Nitrophthal-1-Anilic Acid.—Levi also reports an anilic acid, crystallizing in white needles, melting-point 232°, which does not at all correspond to the pale yellow needles obtained by us, which melt at 180° with formation of the anil. We thought it likely that this acid had the 2-anilic acid form, but Kahn's work makes it seem much more likely that it possesses the 1-anilic acid structure.

3-Nitrophthalamide.—The amide prepared by Levi melted at 219°, while our product melts at 200°-201° with formation of the imide.

4-Nitrophthalanilic Acid.—The anilic acid prepared by Levi

[1] This Journal, **23**, 740-761 (1901).
[2] *Loc. cit.*
[3] *Ber. d. chem. Ges.*, **35**, 3866 (1902).

melted at 204° (uncorr.); our product at 181° with formation of the anil.

4-Nitrophthalimide.—This was prepared by Levi by the action of ammonia upon the anhydride and also by the action of ammonium thiocyanate upon the free acid. His product is apparently the same as that obtained by us subsequently. To the imides of both nitrophthalic acids, Levi assigns the unsymmetrical structure, in the derivatives of the 3-nitro acid placing the imide group (:NH) upon the carbon non-adjacent to the nitro group (a formula, by the way, recently supported by Kahn, in a private communication to one of us).

4-Nitrophthalanil.—Prepared by Levi before either Graebe and Buenzod[1] or ourselves.

4-Nitrophthalamide.—Also prepared by Levi before us.

4-Azophthalic Acid.—Koch[2] obtained an azo acid by the electrolytic reduction of 4-nitrophthalic acid in alkaline solution, and describes the substance as an orange-yellow to rose-red precipitate, decomposing and partly subliming at 200°. We reported two different forms of 4-azophthalic acid: one, by reducing an alkaline solution of 4-nitrophthalic acid with sodium amalgam, was a salmon-colored, crystalline substance not melting below 360°, and giving a silver salt insoluble in hot water; the other, by oxidizing azophthalide with alkaline permanganate solution, separated as a reddish yellow, crystalline precipitate, melting with decomposition at 285°-300°, and yielding a silver salt partly soluble in hot water. The products of all these methods show about the same solubilities in water, alcohol and ether.

It seems not amiss in this connection also to call attention to the fact that 3-nitrophthalic anhydride was prepared by Leupold[3] from the corresponding acid and acetyl chloride three years before Lipschitz[4] reported the same method for the production of the anhydride.

Kahn has recently criticized our method of preparing this anhydride, stating that, in his experience, six to eight hours' heating of the acid at 235°-240° causes considerable decomposition. In his first article[5] he recommends a temperature below 218°, while

[1] *Ber. d. chem. Ges.*, **32**, 1992 (1899).
[2] *Loc. cit.*
[3] Inaugural Dissertation, Basel, 1897, p. 22.
[4] *Monatsh. Chem.*, **21**, 793 (1900).
[5] *Ber. d. chem. Ges.*, **35**, 472 (1902).

in his second[1] he states that a temperature of 230° is about right. As the temperature reported by us (235°-240°) merely represented the temperature of the heating medium, the reaction being conducted in an open flask in the oil-bath, it is probable that the actual temperature of the melt was not far from 230°. We did not determine the temperature of the melt exactly, since our interest lay more in determining the possibility of obtaining the anhydride by heating the acid than in the question of the exact temperature at which the best yield was secured, in view of the fact that Lipschitz[2] shortly before had reported that the anhydride could not be satisfactorily prepared in this way. The fact that the acid is liable to decompose when heated too high was, of course, observed by the earliest workers in this field.[3] Our product, however, was not overheated and showed no signs of decomposition, the solidified melt being light yellow, crystalline and homogeneous. The duration of the reaction, as reported by us (six to eight hours) represented the time consumed in raising the temperature of the oil-bath very gradually until it reached 235°-240°, when no more water was evolved and the flask was removed from the bath. As Kahn has shown, heating for half an hour at 230° is sufficient to complete the reaction.

Concerning the discovery of 3-nitrophthalic acid, the impression might be gathered from certain reference works (Beilstein, Roscoe-Schorlemmer, *et. al.*, in which the name of Marignac precedes that of Laurent, in giving the earliest literature upon the subject, that the work of the former anticipated that of the latter. As a matter of fact, Laurent's work antedated Marignac's by at least a year, as appears from the following: Laurent, in studying the action of nitric acid upon naphthalene, isolated, among other products, an acid which he called "nitrophthalic," and prepared its anhydride, acid ammonium salt and imide. These results were sent to the French Academy of Sciences, on March 16, 1840.[4] By a strange mischance, not only this memoir but four others by the same author upon new compounds of naphthalene were mislaid in the office of the latter journal and lost. When Laurent learned of this loss, he immediately requested De Quesneville to

[1] *Ber. d. chem. Ges.*, **35**, 3859 (1902).

Loc. cit.

[3] Laurent: *Compt. rend.*, **12**, 1193; Marignac: *Ann. Chem.* (Liebig), **38**, 9; Laurent: *Rev. scientif. Indus.*, **6**, 95 and **13**, 602; de Aguiar: *Ber. d. chem. Ges.*, **5**, 899; Kronberg: Inaugural Dissertation, Göttingen, 1881, p. 32, etc.

[4] *Rev. scientif. Indus.*, **5**, 363; **6**, 76-77.

copy the duplicates which had been deposited with the secretary of the Academy and to publish the same in the *Revue scientifique et Industrielle.* This was done, the article appearing four or five months later in Vol. 6, pp. 76-99. Laurent also reported his work upon nitrophthalic acid at the meeting of the Academy, June 21, 1841.[1] Before the publication of Laurent's delayed article in the *Revue scientifique et Industrielle,* a paper appeared in Liebig's *Annalen* (38, 1-13) by Marignac of Geneva, likewise dealing with the action of nitric acid upon naphthalene and announcing the discovery of "nitronaphthalic acid" (identical with Laurent's "nitrophthalic acid") and the preparation of some of its salts. Later in the same year (1841), Laurent[2] called attention to the fact that his work had anticipated Marignac's by at least a year.[3] and so far as we are aware, this claim was never disputed by Marignac. It seems, therefore, that the major portion of the credit for the discovery of nitrophthalic acid belongs to Laurent, not alone because he was actually the first to obtain the acid, but also because Marignac (as he himself acknowledges—*Loc. cit.*) was only following in a line of investigation already largely worked out by Laurent. M. T. BOGERT AND L. BOROSCHEK.

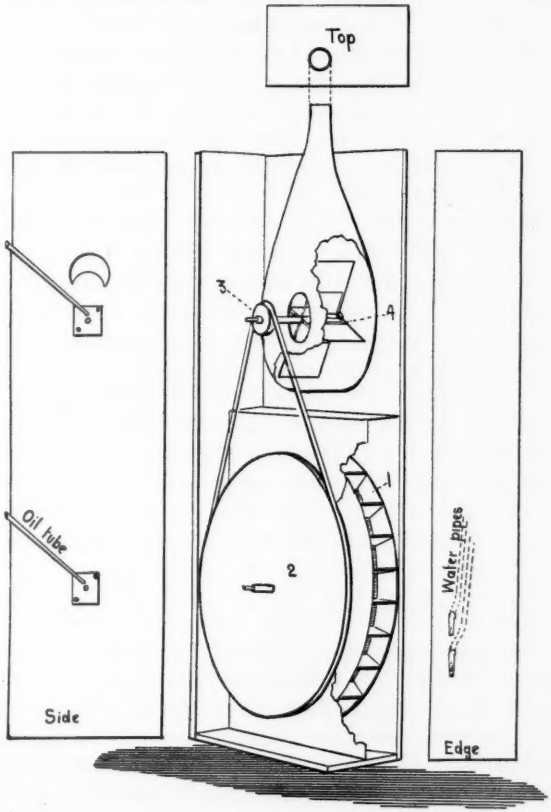
ORGANIC LABORATORY, COLUMBIA UNIVERSITY,
May 14, 1903.

A Cheap and Efficient Water-blast.—The work performed in the chemical laboratory of Cornell College emphasized the necessity of a water-blast, and some of the well-known kinds were purchased. The laboratory is situated on the third floor of the building where the water pressure was found to be scarcely 30 pounds to the square inch. This was not sufficient to maintain the blasts satisfactorily. It was therefore necessary to set about to devise a blast which would be suitable where the water pressure is low and which would give good results with a small jet of water. The apparatus here described has been in use for about four months and seems fully to meet the conditions.

Experiments with various devices were made, but the one that has given the most satisfactory results consists of a small water-wheel (1), a large pulley-wheel (2) connected by belt with a small one (3) for driving a fan wheel (4), all of which are enclosed in a rectangular wooden box 7x12x24 inches.

[1] *Compt. rend.*, **12**, 1193.
[2] *Rev. scientif. Indus.*, **9**, 31.
[3] *Ibid.*, **5**, 363-364.

The water-wheel is 9.5 inches in diameter, and 1.5 inches thick and is made of galvanized iron. Its construction is something on the plan of an undershot wheel. There are twelve paddles on the rim, projecting an inch, against which the water strikes to produce the motion. Each paddle is placed in line with a radius



of the wheel. The larger pulley-wheel has a diameter of 10 inches, is of a good quality of white pine and was soaked for three hours in melted paraffin to prevent warping. It has a groove 3/8 of an inch for the belt. These wheels are mounted on a 3/8 inch shaft, turned down at each extremity to 1/8 inch bearing. The smaller pulley-wheel is of wood 3/4 of an inch in diameter, with flanges

¼ of an inch deep. The fan-wheel consists of four wooden paddles and is 6 inches in diameter. This wheel and the smaller pulley are mounted on a ⅜ inch shaft which is likewise turned down to ⅛ inch journals. The boxings in which the journals run are simply pieces of iron ⅛ of an inch in thickness, with holes drilled to fit the journals, and the iron pieces are fastened to the inside of the case. The water-wheel is separated from the rest of the apparatus by an air-tight tin partition to confine the water, which is conveyed to this wheel by two tubes consisting of mouth-blowpipes cut off at the small extremity to attain an inside diameter of $^{3}/_{32}$ of an inch. These are placed through the edge of the case in such a way that the water from one strikes the paddles just a little below the axis at an angle of 45° to the horizontal plane of this axis, and from the other lower down and nearly parallel to this plane. The best effect is attained when the stream strikes the center of the paddle, when the paddle is exactly at a right angle with the stream. Ordinarily it has been found necessary to employ only one stream of water. Ample provision must be made for the escape of the waste water.

The fan is enclosed in a galvanized iron compartment, and is somewhat like the fan used by the blacksmith. It should have an outlet air tube with an inside diameter of ½ inch. By attaching a Y-tube to this, two blasts can be used as easily as one. A thick-walled rubber tube, about ¼ of an inch in diameter has been found to be the most efficient belt. The bearings must obviously be kept well lubricated to secure easy action.

CHEMICAL LABORATORY, CORNELL COLLEGE, May 8, 1903. FRANK L. HANN.

Rapid Determination of Phosphorus in Steel.—If the yellow precipitate, obtained from 1 gram of drillings, as usual, by shaking in an Erlenmeyer flask, be transferred together with the liquid to a 7-inch test-tube and, after standing one-half hour (a highly essential precaution), be whirled in a centrifugal machine, the supernatant liquid may be poured away and the last drops drained off without any danger of any of the precipitate being carried with it. This is a fact of considerable practical importance as it enables us to dispense with the filtration and prolonged washing which are the most tedious and laborious part of the Handy method. The liquid still adhering to the precipitate and walls of the test-tube after the first decantation and draining, amounts to an error of

about 0.12 per cent. of phosphorus according to Handy's method. But if the test-tube be then nearly filled with water, stoppered and the contents well mixed, again whirled, and the liquid again poured and drained off, the error is reduced to less than 0.001 per cent. The precipitate is then dissolved in standard alkali, and titrated with standard acid as in Handy's method. The Götz method, on account of its inexactness, seems to find but little use. For the method here described, 1 gram of steel is dissolved in 50 cc. of nitric acid (sp. gr. 1.135), the solution boiled, a little solid permanganate added, again boiled, decolorized with sugar or ferrous sulphate, cooled, 10 cc. of strong ammonia and 50 cc. of molybdate solution added, and the mixture shaken as usual in an Erlenmeyer flask. GEORGE AUCHY.

NEW BOOKS.

ELEMENTARY CHEMISTRY. By ROBERT HART BRADBURY, A.M., PH.D., Teacher of Chemistry, Central Manual Training School. Phila., etc. New York: D. Appleton and Company, 1903. Price, $1.25.

The author offers this volume for the use of students in colleges and secondary schools. It consists of two parts—a descriptive portion of 328 pages, and a second part of 157 pages, devoted to the experimental work.

The book is well written and presents its facts clearly and accurately.

The arrangement is that which this particular teacher has found productive of the best results with the students in his charge.

"The theoretical portion is interwoven with the descriptive matter . . . . No generalization is presented until after a particular case of it has been carefully described . . . . More stress is laid upon the mechanism of chemical changes . . . than upon particular facts . . . . It is far more important that the student should understand the behavior of crystal hydrates in general . . . than that he should memorize the number of molecular weights of water in the formulas of innumerable salts."

The author acknowledges his great indebtedness to Ostwald's publications and to the influence upon him of the school of which this scholar is the leading exponent.

The book is well printed and illustrated, containing portraits of Moissan, Priestley, Davy, Rutherford, Lavoisier, Dalton, Wöhler, Liebig, Bunsen and Mendelejeff. It will prove interesting to every teacher of the science and particularly to those who train beginners. EDGAR F. SMITH.

A TEXT-BOOK OF ORGANIC CHEMISTRY. By WILLIAM A. NOYES, Professor of Chemistry in the Rose Polytechnic Institute. New York: Henry Holt & Co. 1903. 534 pp. Price, $1.50.

Among the short text-books of organic chemistry, this appears as a refreshing innovation. Of the extent of but 534 12mo. pages, it manages to compass the relationships of carbon compounds remarkably well. This is done by masterly grouping, and by a prudent distribution of stimulating reading matter. The style of statement is clear, direct and somewhat less technical than the prevalent language of organic chemistry, but the subject is often carried beyond the range of a beginning student of carbon compounds. Some parts of the book seem best adapted to the understanding of those who have already made things in the organic laboratory or have otherwise found their own way in the labyrinth of carbon combination. The question of its use in lectures not preceded by the student's laboratory work is one to be settled by the teacher in actual trial.

Without doubt the book is made the more clear and simple to any learner in that he is given the full benefit of the latest conclusions of research. Every part is freshly written in the light of the present. As instances may be mentioned, the explanation of alcohol and phenol reactions as those of hydroxides on pages 128, 143 and 283; the definition of acids on page 221; the possible structure of crystallized oxalic acid on page 250; esterification in general on pages 279-282; ethers compared with hydroxyl compounds as to their boiling-points on page 284; isocyanide structure on page 305; compounds of a single carbon atom on page 313; the reactivity of halogen compounds of carbon on page 390; the "strength" of organic bases on page 424.

In the division of subject-matter, the hydrocarbons, both aliphatic and aromatic, are brought first into 65 pages, then alcohols with phenols and their ethers are given 44 pages, the aldehydes, ketones and quinones 48 pages, the acids, aliphatic and aromatic, 52 pages. Nitrogen compounds have their more distinct introduc-

tion among the derivatives of the acids. The hydroxy and ketonic acids in 43 pages are followed by the carbohydrates in 22 pages. The descriptive chemistry of halogen compounds is very briefly given, still later.

The work is eminent throughout for its comparative presentation of corresponding reactions and structures, including those seldom grouped together. It is in this way that the attempt modestly acknowledged first in the preface is measurably realized "to present the fundamental facts of organic chemistry for the use of those beginning the subject." But it is in the consolidation of aliphatic and aromatic chemistry that, as said in the preface, "the most radical departure" of the author is made, in the adoption of what appears to him "a more fundamental and logical classification."

That the binary division of carbon chemistry, in use for about thirty years, is suffering numerous complications may be noted by glancing through the outline of ring systems, as in M. M. Richter's "Lexicon," or by a survey of any such class as the terpenes. Many of us who teach have for some time been compelled to present evidence of closed chain structure along with that of open chains, that the student's mind may have the benefit of contrasts and relationships from the first. And it is always a question, how many parallel relations can be carried together with advantage in a given teaching method.

The question has been less serious, when it has been asked, shall the poly-derivatives be all taken along with those of monovalence through the round of oxygen and halogen and nitrogen union, or shall the mono-derivatives be first taken carefully through the stages by themselves? Now the graver question is before us, shall we study together the like derivatives of all the leading orders of hydrocarbons, comparing them all with each other first as hydroxyl compounds, before entering upon their ethers, and so on? Whatever the answer may be in the interest of logical arrangement, to be adopted in handbooks, or in the compilation of abstracts, the teacher will find the necessity of repetition. In organic chemistry the arrangement of matter in the text is seldom found to be just the best consecutive order for presentation in class-work, and this the teacher must decide upon for himself.

As a compact system of the relationships of carbon compounds, having regard to those of greatest interest, within the compass of a

primary text, this work appears to the present writer to be a very valuable contribution. The consolidation of the aliphatic and aromatic divisions is an experiment in the literature well deserving to be made, and we owe thanks to the author.

The tabulation of derivatives is such as to be suggestive to the teacher and convenient for the learner. Much of it is unique, as that of aldehydes and ketones at page 170. At the close of each chapter is a list of the related laboratory exercises. The introductory chapters upon purification, analysis, and molecular weights, and upon the various physical determinations are excellent.

A. B. PRESCOTT.

NOTES ON METALLURGICAL ANALYSIS. BY NATHANIEL WRIGHT LORD, E.M. Second edition rewritten and greatly enlarged. Metallurgical Laboratory, Ohio State University, Columbus, Ohio. Price, $2.50.

The first edition of this work was written for the use of the students in the Ohio State University, and the second edition has been enlarged to a manual covering the greater part of the methods in use in steel works laboratories. Besides the analysis of iron and steel, it contains a chapter on sampling and short descriptions of methods for the assay of copper and zinc ores.

The descriptions of the methods chosen are, as a rule, clear and in sufficient detail, and references are given in many instances to the original papers, which will prove valuable where reference libraries are within reach.

There is no index and as the running head-lines consist of the title of the book, reference to the subject-matter is difficult. There are comparatively few illustrations, and the appearance of the book is poor and lacking in finish. ANDREW A. BLAIR.

QUANTITATIVE CHEMICAL ANALYSIS BY ELECTROLYSIS. BY PROF. ALEXANDER CLASSEN, PH.D., Privy Councillor, Director of the Laboratory of Electrochemistry and Inorganic Chemistry in the Royal Institute of Technology at Aachen. Authorized translation, fourth English from the fourth German edition, revised and enlarged, by BERTRAM B. BOLTWOOD, Ph.D., formerly Instructor in Physical and Analytical Chemistry in the Sheffield Scientific School of Yale University. New York: John Wiley and Sons. 1903. 8vo. vii + 315 pp. 102 illustrations. Price, $3.00.

The name of Professor Classen is so indissolubly connected with the development of electrochemical analysis, and the earlier editions of this book are so favorably known that the present one

is sure of a warm welcome, the more so as it is not merely a translation but a thorough revision which places at the command of English readers the more important results which appeared in Classen's *Ausgewählte Methoden der Analytischen Chemie* (1902), as well as in recent publications by other authors.

The first part, comprising half the book, is devoted to the presentation of the theory and to a description of apparatus and laboratory arrangements. The treatment of the theory is brief (54 pp.), goes directly to the point and is as clear as so condensed a statement can be made. The necessary apparatus is very fully and completely described with the aid of a liberal number of illustrations. The description of the electrical installation of the laboratory at Aix contains many suggestions likely to prove of interest and value to those concerned in introducing new equipment for similar laboratories in this country.

The second part of the book treats of the determination and separation of the metals and halogens. In connection with each topic, references to the literature are given, which, while by no means exhaustive, are sufficiently full for practical purposes. A series of examples are brought together showing the mode of applying electrochemical methods to the analysis of a considerable number of alloys, copper ores, cinnabar, molybdenite, etc.

The labor of the translator is excellently well done, no trace of the German original appearing in the style. A slip, which may be a mere printer's error, occurs in the foot-note on page 281, where "the practical value *in* these examples" is referred to, the author doubtless intending to say *of*. Another typographical error, of which there are not many, is to be found on page 4, where the name of J. B. *Hannay* is printed *Haunay*. A full index, separated after the German fashion into authors and subject, concludes the book, which is one that can not well be dispensed with in any analytical laboratory. LAUNCELOT W. ANDREWS.

PHYSICAL CHEMISTRY FOR PHYSICIANS AND BIOLOGISTS. By DR. ERNST COHEN, Professor of General and Inorganic Chemistry in the University of Utrecht. Authorized translation from the German by MARTIN H. FISCHER, M.D., Instructor on Physiology in the University of California. New York: Henry Holt & Co. 1903. 343 pp.

The book consists essentially of seventeen lectures delivered by Professor Cohen in Amsterdam before a gathering of physicians. The original German edition appeared in 1901 from the press of

Wilhelm Engelmann, Leipzig, and has met with universal favor both at home and abroad.

According to the author: "These lectures are in no way a text-book of physical chemistry." He says further: "I have merely endeavored to show in them the close relation that exists between this new branch of chemistry and the biological sciences, and also, in response to the wishes of my hearers, to describe in some detail the more important methods of physical chemistry."

The treatise does, however, come fully as near satisfying the requirements of such a text-book as do a number of the more pretentious volumes at present available, and may be heartily recommended to a much wider class of readers than is indicated in its title. The theoretical treatment throughout is as rigorous as can fairly be expected in a book of its scope. The author has made free use of the nomenclature of the calculus in the lectures on reaction velocity but the verbal explanations accompanying the formulas make clear in concrete form, the gist of the mathematical processes without burdening the reader with the details of their derivation, and should serve to rob such symbols, when met with in the larger texts or current literature, of much of the mystical element which they too often possess in the eyes of the chemist and biologist. Sufficient of laboratory detail has been introduced to give a strongly objective background to the theoretical part.

The subjects treated in the individual lectures are respectively: 1, Reaction velocity; 2, the inversion of cane-sugar and catalyses in general; 3, the action of ferments; 4, the influence of temperature upon reaction velocity; 5, 6, and 7, equilibrium; 8, the friction of liquids; 9, osmotic pressure; 10, the determination of molecular weight of dissolved substances; 11 and 12, the theory of electrolytic dissociation; 13, 14, and 15, applications; 16, electromotive force; 17, the theory of galvanic elements.

The scope of the applications may be judged from the subheads of 13 to 15 which are: The field of hygiene; disinfection in the light of the theory of electrolytic dissociation; the field of pharmacology; the field of physiology; the osmotic pressure of animal fluids; the osmotic pressure between mother and child; osmotic analysis; poisonous effects. The translator has done his work well, preserving both the form and spirit of the original without unpleasantly warping the English.

It is certainly gratifying to see with what readiness the medical

profession and the general biologist are adopting the methods and results of physico-chemical inquiry. The time seems to have really arrived when it is as necessary to point out the present limitations and tentative character of our methods and conclusions as to urge their more rapid extension to wider fields. The outsider who dips into physical chemistry for cut-and-dried methods to solve his own problems is dangerously apt to carry off a mere shell of formulas without realizing how highly specialized are the "simplifying conditions" upon which they are based. It is far too easy to overlook with what care the particular illustrations in our standard texts have been selected. The physico-chemical problems of biology and medicine are for the most part of a far more complicated character than any as yet systematically investigated in pure chemistry, and we must not be too easily satisfied with superficial analogies. It seems to be a trait of human nature to place most confidence in the results of those studies of which we know the least. Professor Cohen's book should certainly do much toward correcting this tendency in the field with which it deals. There seems at present a great need for just such border-line treatises as the book before us and particularly for those of perhaps even a more pointedly conservative standpoint. The impetus to the new movement has been well given; what it most needs now is careful guidance.

F. G. COTTRELL.

TRAITÉ DE CHIMIE PHYSIQUE. LES PRINCIPES. By JEAN PERRIN. Paris: Librairie Gauthier-Villars. Price, 15 francs.

M. Perrin's book is not by any means what the chemist would expect to find under such a title. Its guiding idea is better suggested by the opening phrase of the preface: "I have gathered together in this first volume the principles whose study and discussion seem to me to form a natural introduction to the different physical sciences." It is not surprising, then, to find that the first half of the book is really a treatise on mechanics and heat, made up largely of what we are accustomed to call mathematical physics, with here and there a paragraph on the chemical aspects of the matter in hand.

As suggested by the quotation above, the author promises more to follow. But he warns us against concluding that the succeeding volumes will be as abstract as the present one. The second is to treat of the application of the phase rule to pure substances and to

mixtures; also of the relations between composition and chemical properties. A further part will include the laws of "diluted matter," in the form of gas, or in solution; also electrochemistry. And a final part will treat of colloidal solutions and the chemical action of radiations.

Judging from the present volume, the work when completed will be one of great interest; for, although in the part before us there is a good deal which for the chemist can only be regarded as good discipline, there are also, here and there, many passages which are suggestive and stimulating; none the less so for the fact that the author's reasoning does not always carry conviction with it. Such is, for instance, that in which an attempt is made to give a more imaginable form to the idea of changes of entropy (Chapter V); and that in which the ordinary idea of forms of energy is discussed (Chapter IV).

The contents of the present volume will be sufficiently indicated by giving the headings of the nine chapters which compose it: I, The notion of force; II, The factors of action; III, The principle of equivalence and the notion of energy; IV, Rôle of the factors of action in the production of changes; V, The principle of evolution; VI, Characteristics of stable equilibrium; VII, Pure substances and laws of combination; VIII, Chemical potential; IX, The phase rule. It will be seen that the later chapters have a much more chemical complexion than the earlier ones; nevertheless the treatment throughout is abstract and mathematical, and will not appeal at all to those chemists to whom the calculus is a stumbling-block. To others this work will hardly fail to be interesting. A. P. SAUNDERS.

DETERMINATION OF RADICALS IN CARBON COMPOUNDS. BY H. MEYER. Authorized translation by J. BISHOP TINGLE. Second edition rewritten. New York: John Wiley and Sons. London: Chapman and Hall. xii + 162 pp. 12mo. Cloth. Price, $1.00.

The first edition of this little book was reviewed in this Journal, **22**, 50, and is already favorably known to organic chemists. The present edition contains over 20 per cent. of new matter, including several cuts. The author has cooperated with the translator in the work of revision. S. P. MULLIKEN.

LOIS GÉNÉRALES DE L'ACTION DES DIASTASES. PAR VICTOR HENRI. Paris: Published by Librairie Scientifique, A. Hermann.

This is a well-printed book of 129 pages devoted to a discussion of the general laws of the action of the diastases.

In the study of the general phenomena of the life of organisms, two groups of theories have been proposed. The theories of the first group regard the vital manifestations as being due to physical and chemical actions only. The theories of the other group admit the existence of forces or energies extra-chemical, so-called vital forces. Since all experimental work with organisms of this kind must be based on physical and chemical principles there is no possibility of demonstrating, by experiment, the value of the theories of the second group. It is self-evident that any so-called vital force is beyond the power of experimental research. The work of Mr. Henri, of course, is based upon the assumption that the theories of the first group are the true ones, and he undertakes the study of the general laws of diastatic actions in their chemical and physical relations. The work is confined to the discussion of three diastases only, namely, invertine, emulsine and amylase. These three diastases have the advantage of lending themselves to experimental study more easily than the other members of the group. While the work is confined almost exclusively to the study of the influence of temperature upon diastatic action it seems possible to base upon it a general theory of diastatic action completely in harmony with the laws of general chemistry.

The work consists of an introduction of twenty-five pages, giving the state of our actual knowledge of catalytic action. The first chapter, eighteen pages, is a historical résumé of the laws of the action of diastases. The second chapter, thirty-three pages, is devoted to the experimental study of invertine. The third chapter, thirteen pages, is devoted to a discussion of the theory of the action of invertine. The fourth chapter, six pages, is devoted to the study of the action of emulsine. The fifth chapter, ten pages, is devoted to the study of the action of amylase upon starch.

The chemical reactions which take place under the influence of these ferments are discussed mathematically and chemically, and this discussion will be a great help to those chemists who desire to apply mathematical formula to chemical processes. The study of catalytic action shows that there are various forms of activity, namely: first, catalysis produced by the simple presence of the ferment; second, autocatalysis; third, formation of intermediate combinations which are produced very rapidly; fourth, intermediate combinations which are produced slowly; fifth, the action of the catalyzing agent upon a series of successive reactions.

In the development of the third class of reactions mentioned above, the theory of E. Fisher is cited. It shows that there is a constant relation existing between the diastase and the chemical constitution of the bodies which are transformed by it. Fisher's theory also holds that, for instance, in the inversion of cane-sugar, there is an actual chemical compound at first formed between the ferment and the sugar, and by the subsequent breaking up of this compound there are formed the invert sugar on the one hand, while the diastase is regenerated on the other. This little work will undoubtedly be of great interest and benefit to those who are pursuing the study of catalytic reactions from theoretical and mathematical points of view. H. W. WILEY.

THE PRINCIPLES OF ANIMAL NUTRITION, WITH SPECIAL REFERENCE TO THE NUTRITION OF FARM ANIMALS. BY HENRY PRENTISS ARMSBY, PH.D., Director of the Pennsylvania State College Agricultural Experiment Station; Expert in Animal Nutrition, United States Department of Agriculture. New York: John Wiley and Sons. 1903. Cloth. 614 pp. Price, $4.00.

The scope of this very readable work is much broader than the second part of the title might suggest to the casual reader, since the various discussions in it apply in most cases to man as well as to the lower animals. From the preface it appears that the substance of the book was first presented to the public as a course of lectures delivered at the Graduate Summer School of Agriculture in Columbus, Ohio, in 1902; in its present expanded form it covers the whole subject in a more systematic manner than would be possible in a course of lectures and is especially characterized by very full references to the original literature.

The general subject is presented under two heads which lead to a division of the book into two parts: 1, The income and expenditure of matter; 2, the income and expenditure of energy. In Part I, which is largely chemical, there are found very clear descriptions of the early experiments of Liebig, Pettenkofer, C. Voit and other pioneer investigators in this field, and also the recent and more exact studies of the modern workers. Chapter V, 92 pages, of this part of the book deals with the question of the relations of metabolism to the food supply and it would not be easy to find a more intelligible or concise presentation of a subject on which the literature has grown to be enormous. This chapter will prove of value to the physiologist or physiological chemist for general

orientation, and through the foot-notes and literature references will serve as a guide for fuller study.

In Part II we find first a short general chapter discussing the relations of force and energy in the animal body and then a chapter on methods of investigating the liberation and transfer of energy. Although necessarily much condensed, this chapter gives a good idea of the construction and use of combustion and respiration calorimeters with discussion of methods of calculation of results. The modern devices of Atwater and others are described fully enough for the needs of the physiologist or general student. Following this chapter on methods there is a short one on the conservation of energy in the animal body and finally four longer chapters on these topics: "The Food as a Source of Energy—Metabolizable Energy"; "Internal Work"; "Net Available Energy—Maintenance"; "The Utilization of Energy". These are well-written and valuable chapters, and while the contents is largely compilation (it could not be otherwise when the magnitude and nature of the topic are considered) the presentation is such as to show the author's full acquaintance with the field and command of the subject. While most of the illustrations in this part of the work are drawn from experiments upon animals, it is clear that the results reached obtain just as certainly for man. The book may therefore be recommended to the attention of those working outside the domain of agricultural chemistry; it must be recognized as a valuable contribution to the literature of physiological chemistry.

J. H. LONG.

TECHNICAL MYCOLOGY: THE UTILIZATION OF MICRO-ORGANISMS IN THE ARTS AND MANUFACTURES. BY DR. FRANZ LAFAR. Translated from the German by CHARLES T. C. SALTER. Vol. II, Part I. Enmycetic Fermentation. London: Charles Griffin and Co. Philadelphia: J. B. Lippincott and Co. 1903. 189 pp.

The first volume of this well-known work appeared in 1898 and was concerned with a discussion of schizomycetic fermentation, or the fermentations and similar changes produced by fusion fungi or bacteria. In the present book, we have the first part of volume second which treats of enmycetic fermentation, or fermentation by the higher fungi, using the term fermentation in the older sense. The book is divided into three sections (Sections X, XI and XII of the whole work). The first treats of the general morphology and biology of the enmycetes; the second of fermentations by species

of the *mucor* family, while the third deals with fermentations by yeast proper.

This last section contains three interesting chapters and is evidently but the introduction to a full discussion of alcoholic fermentation in general, to appear in a later portion of the work. The scope of these chapters is suggested by their titles: Morphology and Life History of Yeasts; The Anatomy of the Yeast Cell; Chemistry of the Yeast Cell. The completed second volume will doubtless prove as useful to chemists interested in fermentation industries as was the first. The mechanical work on the book is excellent. J. H. LONG.

THE AMERICAN YEAR-BOOK OF MEDICINE AND SURGERY. Vol. I. GENERAL MEDICINE. Philadelphia: W. B. Saunders and Co. 1903. 691 pp. Cloth, $3.00 net. Half-morocco, $3.75 net.

This is a valuable annual publication which has already been noticed in this Journal in a review of the volume issued in 1902. The work has not as wide a scope as the *Jahresbericht für Chemie* and the reviews it furnishes are often critical to some degree. But it furnishes an excellent survey of all that is really important in medical literature from the whole world and in readable form. The rapidly increasing importance of chemistry and chemical physiology in general medicine is shown especially in this last volume, which can be recommended to all who are interested in the scientific side of medical progress. The work is issued in two volumes under the editorial control of Dr. George M. Gould. Volume I is always devoted to medicine and Volume II to surgery.

J. H. LONG.

RÉFLEXIONS SUR LA PUISSANCE MOTRICE DU FEU, ET SUR LES MACHINES PROPRES A DÉVELOPPER CETTE PUISSANCE. BY SADI CARNOT. (Réimpression fac-similé conforme a l'édition originale de 1824.) Paris: A. Hermann. 118 pp. 1903.

This reproduction, evidently photographic, of the classic which founded the science of thermodynamics, is a welcome addition to available scientific literature. The original is rarely to be found; and no ordinary reprint, however finely executed, can quite fill its place. One wonders that the photographic method is not more often used for this purpose, for letterpress which has been proof-read by the author has a virtue which no recomposition can attain.[1] The value of this edition is enhanced by an

[1] Ostwald testifies that the present fac-simile is precise, having compared it with his original copy. (*Ztschr. phys. Chem.*, **43**, 640, May, 1903.)

appended facsimile of the page of Carnot's note-book in which his prescience of the mechanical theory and equivalent of heat is recorded, and also by the letter of his brother Senator Carnot to the Academy. These are taken from the French edition of 1878. When following once more, in their original dress, the thoughts of the great pioneer, the reader cannot but wonder concerning the marvels which he might have wrought if his life had ended less prematurely. T. W. R.

INDIA RUBBER AND GUTTA PERCHA, translated from the French of SEALIGMANN, LAMY TORRILHON, AND FALCONNET BY JOHN GEDDES MCINTOSH. London : Scott, Greenwood, and Co. 1903. New York : D. Van Nostrand and Co. Price, $7.50 net.

After an interval of some years in which no comprehensive work on this subject has appeared, two quite elaborate works have appeared almost simultaneously; the one of which the title is given above, and the work of Dr. Carl Otto Weber on "The Chemistry of India Rubber," published this year by Chas Griffin & Co., London, and J. B. Lippincott Co., Philadelphia. The book before us is the more comprehensive in its scope, covering both the subjects India rubber and gutta percha and, as the subtitle states, in their historical, botanical, arboricultural, mechanical, chemical and electrical aspects. As the translator states in his preface, it has been produced by the collaboration of a well-known technical chemist, an equally well-known India rubber manufacturer, and an expert mechanical engineer with special experience of India rubber and gutta percha plant and machinery. Because of this comprehensive plan, the book is a valuable one for those desiring information on the general subject and its different bearings.

The chemistry of the book is not, however, a connected whole written from the standpoint of our present knowledge of the subject, but is in part quite old and somewhat disconnected. As an example we may note the account of dambonite and dambose, the sugar-like body obtained from galoon rubber by Girard. The authors and the translator have preserved the old notation $C_6H_6O_6$ for the sugar and C_2H_3I for methyl iodide, and the only intimation the reader has that these formulas are not to be taken as written is a brief foot-note of the translator to the effect that "all the formulas and equations given by Girard are evidently old notation." We do not think that there is any excuse for

presenting the matter in this shape by a translator who wishes to make the book as thoroughly available as possible. Again, the word hydrocarbide used all through for the English word hydrocarbon is objectionable and is evidently too close a translation of the French "hydrocarbuse." Similar inelegant translation is seen in the use of the word "expiry" instead of "expiration" on p. 97.

Much of the chemical discussion is a reproduction of the views of the original writer given in the first person singular and then with a word of comment, sometimes expressing doubt or dissent, as in the reference of Fawsitt's experiments on vulcanization on p. 137.

The section on the analysis of rubber and rubber substitutes is fairly complete, but is largely given as a quotation from other sources as in the statement of Henrique's contribution.

Taken altogether, the chemical part of the section on India rubber is not as satisfactory in its treatment as that found in Weber's work. The illustrations of this section are also distinctly inferior and many of them so blurred as to make details undistinguishable.

The section on gutta percha is quite complete in the descriptive and botanical parts, but the chemistry of the subject is not as well presented as we find in Obach's fine monograph, which appeared a few years ago in German.

The book conveys a great deal of information but, as shown above, does not seem to present the chemistry of this most interesting subject as well as it might have been done.

SAM'L P. SADTLER.